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(71) Applicant: Matsushita Electric Industrial Co., Ltd.

(72) Inventor: YUASA et al.

(74) Agent: Patent Attorney, Tomoyuki TAKIMOTO et al.

(54) [Title of the Invention] TONER, CARRIER, TWO-COMPONENT DEVELOPER, AND ELECTROPHOTOGRAPHIC METHOD

(57) [Abstract]

[Object] It is an object to provide a toner having high-performance fixing property, developing property, and transfer property, wherein filming on a photoreceptor, a developing member, or the like and a hollow defect in transfer are suppressed, and toner recycle is performed satisfactorily.

[Solving Means] A polyethylene wax or a vegetable wax having specific properties is added and, furthermore, specific relationships are established among the dynamic friction coefficient of an external additive to be added to the toner, the dynamic friction coefficient of a toner base before an external addition treatment, the dynamic friction

coefficient of the toner after the external addition treatment, the specific surface area of the toner base before the external addition treatment, and the specific surface area of the toner after the external addition treatment.

[Claims]

[Claim 1] A toner comprising at least a binder resin, a colorant, and an external additive as main components, the toner being characterized in that the external additive has a dynamic friction coefficient of from 0.12 to 0.30.

[Claim 2] A toner comprising at least a binder resin, a colorant, a wax, and an external additive, the toner being characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, and the external additive has a dynamic friction coefficient of from 0.12 to 0.30.

[Claim 3] A toner comprising at least a binder resin, a colorant, and an external additive as main components, the toner being characterized in that when the dynamic friction coefficient of the external additive is represented as GF and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to a toner base is represented as TF, a relationship represented by a general formula (Mathematical expression 1) is satisfied.

[Mathematical expression 1]

$$GF < TF$$

[Claim 4] A toner comprising at least a binder resin, a

colorant, a wax, and an external additive, the toner being characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, and the external additive has a dynamic friction coefficient of from 0.12 to 0.30, wherein when the dynamic friction coefficient of the external additive is represented as GF and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to a toner base is represented as TF, the relationship represented by the general formula (Mathematical expression 1) is satisfied.

[Claim 5] A toner comprising at least a binder resin, a colorant, and an external additive as main components, the toner being characterized in that when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and a relationship represented by a general formula (Mathematical expression 2) is satisfied.

[Mathematical expression 2]

$$BF < GF < TF$$

[Claim 6] A toner comprising at least a binder resin, a colorant, a wax, and an external additive, the toner being characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, wherein when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and the relationship represented by the general formula (Mathematical expression 2) is satisfied.

[Claim 7] A toner comprising at least a binder resin, a colorant, and an external additive as main components, the toner being characterized in that when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF,

the BET specific surface area of the toner base is represented as SB, and the BET specific surface area of the toner after performing the external addition treatment is represented as ST, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and both the relationship represented by the general formula (Mathematical expression 2) and a general formula (Mathematical expression 3) are satisfied.

[Mathematical expression 3]

$$1.1 < ST/SB < 1.6$$

[Claim 8] A toner comprising at least a binder resin, a colorant, a wax, and an external additive, the toner being characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, wherein when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF, the BET specific surface area of the toner base is represented as SB, and the BET specific surface area of the toner after performing the external addition treatment is represented as ST, BF is from 0.10 to 0.25, GF is from 0.12

to 0.30, and both the relationships represented by the general formulae (Mathematical expression 2) and (Mathematical expression 3) are satisfied.

[Claim 9] A carrier which is a magnetic material having a surface coated with a resin containing an electrically conductive fine powder, the carrier being characterized in that the surface of the coated resin film has a contact angle of from 90 to 120 degrees.

[Claim 10] A carrier which is a magnetic material having a surface coated with a resin containing an electrically conductive fine powder, the carrier being characterized in that the dynamic friction coefficient between the coated resin film and a steel ball is from 0.01 to 0.1.

[Claim 11] A carrier which is a magnetic material having a surface coated with a resin containing an electrically conductive fine powder, the carrier being characterized in that the dynamic friction coefficient between the coated resin film and a toner according to any one of Claims 1 to 8 is from 0.1 to 0.3.

[Claim 12] A two-component developer comprising a mixture of a toner according to any one of Claims 1 to 8 and a carrier according to any one of Claims 9 to 11, the two-component developer being characterized in that the charge rising index in the mixing of the carrier and the toner is from 0.6 to 1.3.

[Claim 13] An electrophotographic method including a toner transfer step of transferring a toner image, which is formed on an image bearer by converting an electrostatic latent image to a visual image, to a transfer material inserted between the image bearer and an electrically conductive elastic roller while applying a transfer bias voltage to the electrically conductive elastic roller, the method being characterized by comprising the step of using a toner according to any one of Claims 1 to 8.

[Claim 14] An electrophotographic method including a toner transfer step of transferring a toner image, which is formed on an image bearer by converting an electrostatic latent image to a visual image, to a transfer material inserted between the image bearer and an electrically conductive elastic roller while applying a transfer bias voltage to the electrically conductive elastic roller, the method being characterized by comprising the step of using a two-component developer composed of a mixture of a toner according to any one of Claims 1 to 8 and a carrier according to any one of Claims 9 to 11 or the two-component developer according to Claim 12.

[Claim 15] An electrophotographic method including a waste toner recycle step of recovering the toner remaining on an image bearer after a transfer process to be reused for a developing process in a developing apparatus, the method

being characterized by comprising the step of using a toner according to any one of Claims 1 to 8.

[Claim 16] An electrophotographic method including a waste toner recycle step of recovering the toner remaining on an image bearer after a transfer process to be reused for a developing process in a developing apparatus, the method being characterized by comprising the step of using a two-component developer composed of a mixture of a toner according to any one of Claims 1 to 8 and a carrier according to any one of Claims 9 to 11 or the two-component developer according to Claim 12.

[Claim 17] An electrophotographic method having a transfer system in which a primary transfer process for transferring a toner image, which is a visualized image of an electrostatic latent image formed on the image bearer, to a surface of an endless intermediate transfer member by bringing the surface of the endless intermediate transfer member into contact with the image bearer is repeatedly performed a plurality of times, and then a secondary transfer process is performed to collectively transfer the superimposed toner images, which are formed on the surface of the intermediate transfer member by repeatedly performing the primary transfer process a plurality of times, to a transfer member, the method being characterized by comprising the step of using a toner according to any one of

Claims 1 to 8.

[Claim 18] An electrophotographic method having a transfer system in which a primary transfer process for transferring a toner image, which is a visualized image of an electrostatic latent image formed on the image bearer, to a surface of an endless intermediate transfer member by bringing the surface of the endless intermediate transfer member into contact with the image bearer is repeatedly performed a plurality of times, and then a secondary transfer process is performed to collectively transfer the superimposed toner images, which are formed on the surface of the intermediate transfer member by repeatedly performing the primary transfer process a plurality of times, to a transfer member, the method being characterized by comprising the step of using a two-component developer composed of a mixture of a toner according to any one of Claims 1 to 8 and a carrier according to any one of Claims 9 to 11 or the two-component developer according to Claim 12.

[Claim 19] An electrophotographic method characterized by comprising the step of using a toner according to any one of Claims 1 to 8 for a color electrophotographic apparatus including a plurality of movable image formation units having at least respective rotating image bearers and developing devices with toners of mutually different colors to form mutually different color toner images on the

respective image bearers; an image formation position composed of a single exposure position and a single transfer position; an image formation unit group in which the plurality of image formation units are placed annularly; a movement device for rotationally moving the entire image formation unit group to sequentially move the individual image formation units to the single image formation position; a light irradiating device for emitting signal light; and a mirror which is located at substantially the center of rotation of the rotational movement of the above-described image formation unit group for guiding the light from the light irradiating device to the exposure position, wherein a color image is formed by transferring the different color toner images to a transfer material while the toner images are registered and superimposed.

[Claim 20] An electrophotographic method characterized by comprising the step of using a two-component developer composed of a mixture of a toner according to any one of Claims 1 to 8 and a carrier according to any one of Claims 9 to 11 or the two-component developer according to Claim 12 for a color electrophotographic apparatus including a plurality of movable image formation units having at least respective rotating image bearers and developing devices with toners of mutually different colors to form mutually different color toner images on the respective image

bearers; an image formation position composed of a single exposure position and a single transfer position; an image formation unit group in which the plurality of image formation units are placed annularly; a movement device for rotationally moving the entire image formation unit group to sequentially move the individual image formation units to the single image formation position; a light irradiating device for emitting signal light; and a mirror which is located at substantially the center of rotation of the rotational movement of the above-described image formation unit group for guiding the light from the light irradiating device to the exposure position, wherein a color image is formed by transferring the different color toner images to a transfer material while the toner images are registered and superimposed.

[Claim 21] The toner according to any one of Claims 1 to 8, or the toner, the two-component developer, or the electrophotographic method according to any one of Claims 12 to 20, characterized in that the external additive to be added to the toner comprises at least one of silicon oxide fine powders, titanium oxide fine powders, magnetite fine powders, titanate fine powders, zirconia acid salt fine powders, and tungsten carbide fine powders.

[Claim 22] The toner according to any one of Claims 1 to 8, or the toner, the two-component developer, or the

electrophotographic method according to any one of Claims 12 to 20, characterized in that the vegetable wax to be added to the toner is at least one member selected from the group consisting of carnauba waxes having a melting point based on the DSC method of from 80°C to 86°C, candelilla waxes having that of from 68°C to 72°C, hydrogenated jojoba oils having that of from 66°C to 72°C, and rice waxes having that of from 79°C to 83°C.

[Claim 23] The toner according to any one of Claims 1 to 8, or the toner, the two-component developer, or the electrophotographic method according to any one of Claims 12 to 20, characterized in that the polyethylene based wax to be added to the toner is produced by a pyrolysis method has a recovery rate of 95% or more when being washed with toluene at 25°C for 1 hour.

[Claim 24] The toner according to any one of Claims 1 to 8, or the toner, the two-component developer, or the electrophotographic method according to any one of Claims 12 to 20, characterized in that the binder resin serving as a main component of the toner comprises a styrene (meth)acrylic acid alkyl ester copolymer having a weight average molecular weight Mw of from 100,000 to 500,000, a ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn of from 40 to 90, a ratio Mz/Mn of the Z average molecular weight Mz to the number

average molecular weight Mn of from 350 to 900, and a 1/2 outflow temperature measured by Koka type flow tester of from 105°C to 145°C.

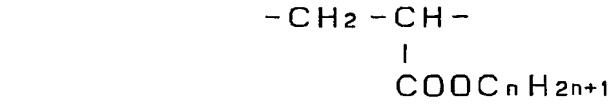
[Claim 25] The toner according to any one of Claims 1 to 8, or the toner, the two-component developer, or the electrophotographic method according to any one of Claims 12 to 20, characterized in that the binder resin serving as a main component of the toner comprises a polyester resin having a weight average molecular weight Mw of from 10,000 to 300,000, a ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn of from 3 to 50, a ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn of from 10 to 800, a 1/2 outflow temperature measured by Koka type flow tester of from 80°C to 150°C, and a flowing start temperature of from 80°C to 120°C and being produced by polycondensation of a polyvalent carboxylic acid or a lower alkyl ester thereof with a polyhydric alcohol.

[Claim 26] The carrier, the two-component developer, or the electrophotographic method according to any one of Claims 9, 10, 11, 12, 14, 16, 18, and 20, characterized in that the resin constituting the coated layer of the carrier comprises at least one member selected from the group consisting of silicone resins and acrylic resins.

[Claim 27] The carrier, the two-component developer, or the

electrophotographic method according to any one of Claims 9, 10, 11, 12, 14, 16, 18, and 20, characterized in that the resin constituting the coated layer of the carrier comprises at least a resin formed from an alkyl (meth)acrylate polymer including a long alkyl chain which is represented by (Chemical formula 1) and which includes 14 to 26 carbon atoms.

[Chemical formula 1]



(where n represents 14 to 26)

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to toner used for copying machines, printers, and facsimiles.

[0002]

[Description of the Related Art] In recent years, electrophotographyic apparatuses, which have been used in offices, have been used increasingly for personal purposes, and therefore technologies of miniaturization, maintenance free, and the like have been required therefor. Consequently, needs such that maintenance properties, such as recycling of waste toner, are improved, emission of ozone is reduced, and the like exist.

[0003] The printing processes of electrophotographic copying machines and printers will be described. First, an image bearer (hereinafter, referred to as a photoreceptor) is electrostatically charged for forming an image. Examples of charging methods include a method in which a conventionally used corona electric charger is used and a method which is used in recent years and in which a surface of a photoreceptor is uniformly charged by, for example, a contact type charging method through direct pressing of an electrically conductive roller against the photoreceptor, for the purpose of reducing the amount of generation of ozone. In a copying machine, after the photoreceptor is electrostatically charged, an original to be copied is irradiated with light. The photoreceptor is irradiated with the reflected light through a lens system. In a printer, an image signal is transmitted to a light-emitting diode or a laser diode serving as a light source, and a latent image is formed on a photoreceptor by ON-OFF control of light. When the latent image (variation in surface potential) is formed on the photoreceptor, the photoreceptor is converted to a visible image by a toner (having a diameter of from about 5 μm to 15 μm) which is a colored powder electrostatically charged in advance. The toner adheres to the surface of the photoreceptor depending on the levels of surface potentials of the photoreceptor, and is electrically transferred to the

copying paper. More specifically, since the toner is positively or negatively charged in advance, and the backside of the copying paper is charged with a polarity opposite to the polarity of the toner, the toner is attracted electrically. As for the transfer method, a method in which a conventionally used corona electric charger is used and a transfer method which is used in recent years and in which an electrically conductive roller is directly pressed against the photoreceptor for the purpose of reducing the amount of generated ozone have been put into practical use. In the transfer process, all the toner on the photoreceptor is not transferred to the copying paper, and a part of the toner remains on the photoreceptor. The remaining toner is scraped off by a cleaning blade or the like in a cleaning section and waste toner is produced. The toner transferred to the copying paper is fixed to the paper by heat or pressure in a fixing step.

[0004] It is well known that the toner for electrostatic charge developing used in the electrophotographic method is generally composed of a resin component, a coloring component formed from a pigment or a dye, a plasticizer, a charge controlling agent, and if necessary, additive components, such as magnetic materials and releasing agents. For the resin component, a natural or a synthetic resin is used alone or in combination.

[0005] The above-described additives are pre-mixed in an appropriate ratio and the resulting mixture is heated and kneaded through heat melting. The mixture is then pulverized by an air-stream type collision plate system or the like. The resulting fine powder is classified so as to complete a toner base. Thereafter, an external additive is added externally to the toner base to prepare a toner.

[0006] In a single-component development, the developer is composed of a toner alone. However, a two-component developer is prepared by mixing a toner with a carrier composed of magnetic particles.

[0007] In a color copying machine, the photoreceptor is electrostatically charged by corona discharge using an electric charger. Thereafter, a latent image for each color is prepared by irradiating the photoreceptor with a light signal. The latent image is developed with a first color toner, for example, a yellow toner, and therefore, the latent image is converted to a visible image. Subsequently, a transfer material charged with a polarity opposite to that of the charge of the yellow toner is brought into contact with the photoreceptor, so that the yellow toner image formed on the photoreceptor is transferred thereto. The photoreceptor is cleaned by removing the toner remaining after the transfer process, and then discharged, resulting in completion of developing and transferring of the first

color.

[0008] Thereafter, the same operation as that for the yellow toner is repeated for toners of magenta, cyan, and the like. The thus prepared different color toner images are superimposed on the transfer material to form a color image. The resulting superimposed toner images are transferred to the transfer paper charged with a polarity opposite to that of the toner and then fixed, resulting in completion of copying.

[0009] Examples of general methods for forming a color image include a transfer drum system and a sequential superimposition system. In the transfer drum system, toner images of individual colors are formed on a single photoreceptor sequentially, and a transfer material wound on a transfer drum is allowed to face the photoreceptor repeatedly by being rotated, so that the toner images of individual colors formed sequentially are superimposed and transferred. In the sequential superimposition system, a plurality of image formation sections are disposed sequentially, and a transfer material transported by a belt is passed through the individual image formation sections and the toner images of individual colors are transferred sequentially to the transfer material, so that the color images are superimposed.

[0010] One example using the above-described transfer drum

system is a color image formation apparatus disclosed in Japanese Unexamined Patent Application Publication No. 1-252982. Fig. 5 is a schematic diagram of an entire configuration of this conventional example. The configuration and the operation thereof will be described below briefly. In Fig. 5, reference numeral 501 denotes a photoreceptor. An electric charger 502, a developing section 503, a transfer drum 504, and a cleaner 505 are disposed so as to face the photoreceptor 501. The developing section 503 is composed of a Y developing unit 506 for forming a yellow toner image, an M developing unit 507 for magenta, a C developing unit 508 for cyan, and a Bk developing unit 509 for black. The entire developing unit group is rotated in such a way that the individual developing units are allowed to face the photoreceptor 501 sequentially to become ready for developing. The transfer drum 504 and the photoreceptor 501 are rotated at constant rates in their respective arrow directions while facing each other during the operation.

[0011] When an image formation operation is started, the photoreceptor 501 is rotated in the arrow direction and, in addition, the surface thereof is uniformly charged with the electric charger 502. Thereafter, the surface of the photoreceptor is irradiated with a laser beam 510 which has been modulated with a signal for forming an image of a first

color, yellow, resulting in formation of a latent image. The resulting latent image is first developed by the Y developing unit 506 facing the photoreceptor 501 to form a yellow toner image. By the time when the yellow toner image formed on the photoreceptor is moved to a position facing the transfer drum 504, an end of a sheet of paper serving as a transfer material and fed from a paper supply section 511 has been trapped by a hook 512 and wound around an outer perimeter of the transfer drum 504. Thus, timing is adjusted in such a way that the yellow toner image on the photoreceptor faces and meets a predetermined position of the paper.

[0012] After the yellow toner image on the photoreceptor is transferred to the paper by the function of a transfer electric charger 513, the surface of the photoreceptor is cleaned by the cleaner 505, so that the surface becomes ready to the next image formation. Subsequently, the toner images of magenta, cyan, and black are formed similarly. At this time, the developing section 503 allows individual developing units 506 to 509, which are used for forming respective color images, to face the photoreceptor so as to become ready for developing. The diameter of the transfer drum has a sufficient size to allow the longest paper to be wound around the drum and to make it possible to exchange the developing units between formations of different color

images.

[0013] The laser beam 510 for forming the images of individual colors is applied while the timing is adjusted in such a way that the toner images of individual colors on the photoreceptor are transferred to desired positions and face the toner image which has been transferred to the paper on the transfer drum. In this manner, toner images of four colors are superimposed and transferred to the paper on the transfer drum 504, resulting in formation of a color image on the paper. After all the toner images of individual colors are transferred, the paper is peeled off from the transfer drum 504 by a peeling hook 514. After the resulting paper is passed through a transport section 515, the toner image is fixed thereon by a fixing unit 516, and the paper is output to the outside of the apparatus.

[0014] On the other hand, Japanese Unexamined Patent Application Publication No. 1-250970 discloses an example of a color image formation apparatus by using the sequential transfer system. In this conventional example, for the purpose of forming images of four colors, four image formation stations each including a photoreceptor, light-scanning device, and the like are arranged and the paper transported by a belt is passed through a lower portion of each photoreceptor and, thereby, color toner images are superimposed.

[0015] Furthermore, Japanese Unexamined Patent Application Publication No. 2-212867 discloses another method for forming a color image by superimposing toner images of different colors on a transfer material. In this method, toner images of individual colors formed sequentially on a photoreceptor are once superimposed on an intermediate transfer material, and finally, the toner images on the intermediate transfer material are transferred collectively to the transfer paper.

[0016]

[Problems to be Solved by the Invention] Recently, from the view point of global environmental protection, the needs for reuse of waste toner, which has been disposed of without being reused, and a low-temperature fixing method which reduces the power consumption in fixing have been intensified in order to reduce the amount of generation of ozone or regulate unlimited industrial waste disposal. Toner materials have also been improved in order to respond to a roller transfer method in which the amount of generation of ozone is reduced, recycling in which waste toner is reused, and lower-temperature fixing. In a production process of toner, a toner fine powder generated in fine powder classification is disposed of without being reused under present circumstances. This is because if the fine powder is returned to a mixing step or a kneading step

to be reused, the mixing and kneading properties deteriorate, resulting in uneven dispersion of an internal additive and, therefore fog on a copied image and toner scattering tend to occur. Therefore, this reuse of the fine powder toner in the classification is also an important issue. Furthermore, it is an important issue from the view point of environmental protection to provide a high-performance toner capable of satisfying a plurality of items simultaneously instead of a toner satisfying only one of the items.

[0017] In copying machines, printers, and facsimiles, different types of toners are used depending on the process speed thereof. For example, for a low-speed machine, a high-viscoelasticity, high-softening point binder resin material is used in order to improve the offset resistance. For a high-speed machine, since it is difficult to ensure an amount of heat required for fixing, another binder resin having different properties, in which the softening point is lowered to improve the fixing property, is used. The process speed of a machine is linked with the copying treatment capacity per hour of the machine, and indicates the circumferential speed of the photoreceptor thereof. The transport speed of copying paper is determined on the basis of the circumferential speed of the photoreceptor. If these different toners can be replaced with one toner, the productivity is increased and the toner cost can be

decreased drastically.

[0018] In a fixing step, the fixing strength that is adhesion of a toner to paper and the offset resistance for preventing adhesion to a heat roller are control factors.

[0019] The toner is melted and penetrates into fibers of the paper by heat or pressure from a fixing roller and, thereby, the fixing strength is attained. In order to increase this fixing strength, heretofore, binder resins have been improved and releasing agents and the like have been added, so that the fixing strength of the toner to the paper is increased and an occurrence of offset phenomenon, in which a toner is adhered to a fixing roller, is prevented.

[0020] Japanese Unexamined Patent Application Publication No. 59-148067 discloses a toner in which an unsaturated ethylene based polymer having a low molecular weight portion and a high molecular weight portion, a specific peak value in the low molecular weight, and a specific Mw/Mn ratio is used as a resin and a polyolefin having a specific softening point is contained. It is described that the fixing property and the offset resistance are thereby ensured. Japanese Unexamined Patent Application Publication No. 56-158340 discloses a toner containing a resin composed of specific low molecular weight polymer component and high molecular weight polymer component as a main component. The purpose of this is to ensure the fixing property by the low

molecular weight component and ensure the offset resistance by the high molecular weight component. Japanese Unexamined Patent Application Publication No. 58-223155 discloses a toner in which a resin composed of an unsaturated ethylene based polymer having relative maximum values in molecular weight ranges of from 1,000 to 10,000 and from 200,000 to 1,000,000 and a Mw/Mn ratio of from 10 to 40 and a polyolefin having a specified softening point. It is used for the purpose of ensuring the fixing property by using the low molecular weight component and ensuring the offset resistance by using the high molecular weight component and the polyolefin.

[0021] However, if a resin, in which the melt viscosity of the binder resin is decreased or the molecular weight is decreased, is used for increasing the fixing strength in a high-speed machine, so-called "spent" in that a toner is adhered to a carrier, tends to occur during a long period of use for a two-component development. For a single-component development, a toner tends to adhere to a doctor blade or a developing sleeve, and thereby the stress resistance of the toner is reduced. If it is used in a low-speed machine, offset in that a toner is adhered to a heat roller during fixing tends to occur. In addition, blocking in that toner particles are fused with each other occurs during a long period of storage.

[0022] Although the fixing strength and the offset resistance may become compatible with each other in a narrow process speed range by taking a configuration such that a high molecular weight component and a low molecular weight component are blended, it is difficult to respond to a wide range of process speeds. In order to respond to a wide range of process speeds, a configuration composed of a higher molecular weight component and a lower molecular weight component is required. In a high-speed machine, the fixing strength can be increased by increasing the low molecular weight component. However, the offset resistance is deteriorated. In a low-speed machine, an effect of improving the offset resistance is exerted by increasing the high molecular weight component. However, if the high molecular weight component is increased, problems occur in that the pulverization property of the toner is deteriorated and the productivity is reduced. On the other hand, when a low melting point releasing agent, for example, a polypropylene wax is added, to a configuration in which the high molecular weight component and the low molecular weight component are blended or copolymerized, the property of releasing from the heat roller in fixing is improved, and thereby an effect of improving the offset resistance can be exerted. Furthermore, when a polyethylene wax or a natural wax, e.g., a carnauba wax, a rice wax, a candelilla wax, or

a jojoba wax, is added, the fixing property can be improved even when the amount of the low molecular weight component contributing to the fixing property of the binder resin is the same because the wax itself has an effect of penetrating into paper and a friction reduction effect, and the wax is melted and deposited on a toner surface by the heat during the fixing. That is, the fixing property improvement action due to addition of the polyethylene wax or the like is resulted from not only the effect of increasing the strength of bonding between the copying paper and the toner, but also the effect of relieving a force from the outside.

[0023] However, when using the above-described materials having high releasing property, a toner with opposite polarity tends to be generated and the quality is deteriorated unless the materials have good dispersibility in the binder resin. Furthermore, there is a problem in that the carrier, the photoreceptor, and the developing sleeve are polluted by a film thereof. In addition, due to the sliding effect of a wax, it becomes unable to remove low resistance substances adhered to a photoreceptor with a cleaning blade, an electric charge on the surface of the photoreceptor flows at high humidities, resulting in formation of image defects.

[0024] When the slippiness of the toner is varied, the mixing property thereof with the carrier may be varied, the

charge rising property may be affected, and oppositely charged particles may be increased. Furthermore, the carrier surface is coated with a resin having low surface energy for taking measure against so-called "spent" in that a low melting point component of a toner is adhered to the carrier surface. The slippiness of the carrier against the toner may be varied by the coated resin, and thereby the charge rising property may be deteriorated, and background fogging may be increased.

[0025] A releasing agent is microdispersed in the binder resin in a kneading step. The dispersion state thereof influences not only on the fixing property and the offset property of the toner, but also on the electrostatic charge property. If the dispersibility is deteriorated, uneven distribution or liberation of the additive occurs in a resin and, thereby background fogging is increased due to increase of oppositely charged particles. In addition, problems occur in that the offset resistance is deteriorated due to liberation of the additive, and the photoreceptor and the developing sleeve are polluted. In particular, in a resin which is composed of a low molecular weight component and a high molecular weight component and which has a wide molecular weight distribution, poor dispersion of an additive tends to occur more easily. When kneading is performed at low temperatures, the high molecular weight

component is not adequately melted, and therefore poor dispersion of the additive may occur or molecule cleavage of the high molecular weight component may occur due to application of a significant stress to the resin, resulting in reduction of the molecular weight. If the kneading is performed at high temperatures, the viscosity of the low molecular weight component is lowered, and thereby it becomes difficult to apply a stress for kneading. Consequently, poor dispersion may occur and it becomes difficult to adjust the balance between the temperature and the dispersibility.

[0026] As described above, from the view point of global environmental protection in recent years, it is preferable that the waste toner, which has remained on a photoreceptor after a transfer process and has been recovered with a cleaning device, is reused for the developing step again. However, in recycling of waste toner, a soft portion of the toner where a releasing agent is present is damaged by a stress or the like applied to the waste toner in a cleaner section, a developing section, or a transport pipe used for returning the waste toner to the developing section. When the waste toner scraped off from the photoreceptor in the cleaning step is reused in developing, and the waste toner exhibiting poor dispersion is mixed with a fresh toner in the developing unit, the distribution of the amount of

electrostatic charge becomes uneven, and thereby the toner with the opposite polarity is increased, resulting in deterioration of image qualities. Furthermore, filming of a wax on the photoreceptor is promoted, resulting in reduction of life. A paper with short length, e.g., a postcard, is transported by a friction force between a photoconductor drum and the paper. When the above-described releasing agent is adhered to the photoreceptor, the transport force thereof is reduced, and the postcard cannot be satisfactorily passed through.

[0027] In the above-described transfer system by using an electrically conductive elastic roller, a transfer paper is inserted between an image bearer and the electrically conductive elastic roller, and a transfer bias voltage is applied to the above-described electrically conductive elastic roller, so that the toner on the above-described image bearer surface is transferred to the transfer paper. In the transfer system including such an electrically conductive elastic roller, there is a problem in that pollution of backside of the transfer paper occurs. This mechanism is as follows. In the case where the toner on the image bearer is transferred to the transfer paper by using the transfer roller while the transfer paper is not present, the transfer roller is in contact with the image bearer at a predetermined pressure. If fog occurs frequently in the

developing step, the transfer roller is polluted with the toner resulting from such fog, and the transfer roller polluted with the toner is brought into contact with the back surface of the transfer paper transported there, resulting in occurrence of backside fogging.

[0028] As described below, the electrophotographic method by using the toner according to the present invention has a configuration in which an intermediate transfer member is used.

[0029] In the transfer drum system, a transfer drum is used for registering and superimposing toner images of different colors. This transfer drum is rotated at the same speed as that of the photoreceptor. Furthermore, in the case where a color image is formed, the positions of individual color toner images are registered relative to each other by timing the front ends of the images to each other. However, in the above-described configuration, since the paper must be wound around the transfer drum, the diameter of the transfer drum must be at least a predetermined size. In addition, since a very complicated and highly precise structure is required, the apparatus becomes extensive and expensive. Tough paper, e.g., a postcard or thick paper, cannot be wound around the transfer drum and, therefore, cannot be used.

[0030] In contrast, a sequential transfer system includes plural image formation positions, the number of which

corresponds to the number of colors through which a paper is passed sequentially. Therefore, the above-described transfer drum is not required. However, in this system, a plurality of latent image formation devices, e.g., laser optical systems to form a latent image on the photoreceptor, the number of which corresponds to the number of colors are required. Consequently, the structure is very complicated and expensive. Since there are a plurality of image formation positions, positional deviation of image formation sections of individual colors relative to each other, eccentricity of a rotation axis, deviation in parallelism of individual sections, and the like exert direct influences on color misalignment, it has been difficult to stably achieve high image qualities. In particular, registration among individual colors of latent images produced by the latent image formation device must be performed precisely. Therefore, as is also shown in Japanese Unexamined Patent Application Publication No. 1-250970, there is a problem in that the image irradiation system serving as the latent image formation device has to be considerably improved and therefore the system has a complicated configuration.

[0031] In the example including an intermediate transfer member disclosed in Japanese Unexamined Patent Application Publication No. 2-212867, toner images of individual colors must be formed on the same photoreceptor. Consequently, a

plurality of developing units must be disposed in the periphery of a single photoreceptor. Inevitably, the shape of the photoreceptor is upsized and the photoreceptor takes on the shape of a hard-to-handle belt. When each developing unit is exchanged in a maintenance, adjustment of the developing unit may be required to match the developing unit to the properties of the photoreceptor. In addition, when the photoreceptor is exchanged, positional adjustment may be required between individual developing units and the photoreceptor. Therefore, it is difficult to perform maintenance on the individual developing units and the photoreceptor.

[0032] However, the intermediate transfer system is in no need of a complicated optical system and can be used for tough paper, e.g., a postcard or thick paper. In addition, when an intermediate transfer belt is used, there is a merit that the apparatus itself may be miniaturized as compared with the transfer drum system and sequential transfer system because the intermediate transfer belt has good flexibility.

[0033] Although it is ideal that all toner is transferred during the transfer, a part thereof remains after image transfer. Namely, the transfer efficiency is not 100%, but generally is about 75% to 90%. The toner remaining after image transfer is scraped off by a cleaning blade or the like in a photoreceptor cleaning step, resulting in

formation of waste toner.

[0034] However, in the configuration including an intermediate transfer member, the toner is subjected to the transfer step at least two times, that is, from the photoreceptor to the intermediate transfer member and, furthermore, from the intermediate transfer member to the transfer paper. Therefore, even when the transfer efficiency is, for example, 85% in an usual copying machine with one time of transfer, the transfer efficiency is decreased to 72% after two times of transfer. Furthermore, if the transfer efficiency is 75% after one time of transfer, the transfer efficiency is decreased to 56%, and about a half of the toner becomes waste toner. Consequently, the cost of toner is increased, and the volume of a waste toner box must be increased, so that the apparatus cannot be miniaturized. The factor of the reduction in transfer efficiency is believed to be background fogging with an opposite polarity or transfer dropout due to poor dispersion.

[0035] In color image developing, since four color toner images are superimposed on a photoreceptor, the thickness of the toner layer is increased, and a pressure difference tends to occur between a thick toner layer and a portion where no toner layer is present or a thin toner layer is present. Consequently, a "hollow defect" phenomenon in that a part of an image is not transferred and a hole is formed

due to agglomeration effect of the toner, tends to occur. When a material exhibiting high toner-releasing effect is used as the intermediate transfer member to reliably perform the cleaning and a transfer paper jam occurs, hollow defects occur remarkably, and the quality of the image is deteriorated significantly. In a character, a line or the like image, an edge effect is exhibited, and a large amount of toner is adhered thereto. Therefore, toner particles are agglomerated with each other by application of pressure, and hollow defects occur more remarkably. In particular, hollow defects occur more remarkably in a high-humidity and high-temperature environment.

[0036] As described below, the electrophotographic method using the toner according to the present invention has a configuration in which a plurality of movable image formation units for forming toner images of different colors are placed annularly so as to constitute an image formation unit group, and the whole of the image formation units is rotationally moved. Furthermore, in the configuration, exchange can be performed on an image formation unit or intermediate transfer unit basis. When the life thereof expires and the time of exchange is reached, maintenance can easily be performed by exchanging on a unit basis. Therefore, even an electrophotographic color printer can exhibit black-and-white printer-level maintainability.

However, since the image formation unit itself revolves, cleaned waste toner is temporarily and repeatedly adhered to the photoreceptor, and is repeatedly released from and adhered to the developing roller. Consequently, damage to the photoreceptor or filming tends to occur. If the charge rising property is poor in an initial stage of developing, initial fogging is induced.

[0037] When fixing this four color toner images, color mixing of the color toners must be performed. At this time, if poor melting of the toner occurs, scattering of light occurs on the surface or in the inside of the toner image, the color tone inherent in the toner colorant is impaired and, in addition, the light does not incident to the lower layer of the superimposed portion, resulting in deterioration of the color reproducibility. It is necessary for the toner to have a complete melt property and to have a light transmitting property to such an extent as not to deteriorate the color tone. However, when the resin has the above-described configuration and an improvement of the melting property is intended, the offset resistance is deteriorated. All the toner is not fixed to the paper, but is also adhered to the fixing roller surface, resulting in occurrence of offset. Consequently, when the offset resistance is improved by adding a releasing agent, such as polypropylene or polyethylene, the color becomes muddy, and

the color reproducibility is deteriorated.

[0038] Japanese Unexamined Patent Application Publication No. 5-119509 and Japanese Unexamined Patent Application Publication No. 8-220808 report that excellent fixing property and excellent offset resistance are obtained while preventing the color from becoming muddy by adding a large amount of carnauba wax.

[0039] As described above, however, if a low-melting point wax, e.g., carnauba wax, or the like is added, low-resistance substances adhered to the photoreceptor cannot be removed, and occurrence of filming on a photoreceptor or an intermediate transfer member or faulty transfer is induced. Furthermore, these phenomena become remarkable in a waste toner recycle process.

[0040] In consideration of the above-described problems, it is an object of the present invention to provide a toner having a property such that low-resistance substances adhered to a photoreceptor can easily be removed, and furthermore, an occurrence of filming on a photoreceptor or an intermediate transfer member and faulty transfer can be prevented even when the toner includes an internal additive, e.g., low-melting point wax, dispersed in a binder resin.

[0041] It is also an object to provide a full-color electrophotography toner which can be used for oil-less fixing in which no oil is applied.

[0042] It is also an object to provide a toner having a uniform electrostatic charge distribution even when the toner has a configuration such that an internal additive, e.g., wax, having high releasing property and high slippiness is contained in a binder resin.

[0043] It is also an object to provide a toner having good combination of fixing property and offset resistance even when used for a model in which the process speed is varied in a wide range, excellent dispersibility and stable electrostatic charge property, while producing high quality images.

[0044] It is also an object to provide a toner capable of preventing occurrence of hollow defect or scattering during image transfer in an electrophotographic method using an electrically conductive elastic roller or an intermediate transfer member and obtaining a high transfer efficiency.

[0045] It is also an object to provide a developer having a property such that filming on a photoreceptor or an intermediate transfer member is prevented even during a long period of use, and no image deletion occurs even under high humidity conditions.

[0046] It is also an object to provide a developer having a property such that the amount of electrostatic charge and the fluidity are not reduced even when a waste toner is recycled, no agglomerate is generated, the life thereof is

extended, recycle developing is made possible, and prevention of global environmental pollution and reuse of the resource are made possible.

[0047] It is also an object to provide a developer having a property such that uniform dispersion can be kept even when a fine powder toner generated in the fine powder classification in a manufacturing process is reused, and reuse of the resource is made possible.

[0048]

[Means for Solving the Problems] As the first configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, and an external additive as main components and which is characterized in that the external additive having a dynamic friction coefficient of 0.12 to 0.30 is contained.

[0049] As the second configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, a wax, and an external additive and which is characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, and the external additive has a dynamic friction coefficient of from 0.12 to 0.30 while the toner has a dynamic friction

coefficient of from 0.15 to 0.35.

[0050] As the third configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, and an external additive as main components and which is characterized in that when the dynamic friction coefficient of the external additive is represented as GF and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to a toner base is represented as TF, the relationship, GF < TF, is satisfied.

[0051] As the fourth configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, a wax, and an external additive and which is characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, and the external additive has a dynamic friction coefficient of from 0.12 to 0.30, wherein when the dynamic friction coefficient of the external additive is represented as GF and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to a toner base is represented as TF, the relationship, GF < TF, is satisfied.

[0052] As the fifth configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, and an external additive as main components and which is characterized in that when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and a relationship represented by a general formula (Mathematical expression 1) is satisfied.

[0053] As the sixth configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, a wax, and an external additive and which is characterized in that the wax is composed of at least one kind of vegetable wax having a melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, wherein when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to

the toner base is represented as TF, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and the relationship represented by the general formula (Mathematical expression 1) is satisfied.

[0054] As the seventh configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, and an external additive as main components and which is characterized in that when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF, the BET specific surface area of the toner base is represented as SB, and the BET specific surface area of the toner after performing the external addition treatment is represented as ST, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and both the relationship represented by the general formula (Mathematical expression 1) and a general formula (Mathematical expression 2) are satisfied.

[0055] As the eighth configuration of the toner according to the present invention, a toner is provided which contains at least a binder resin, a colorant, a wax, and an external additive and which is characterized in that the wax is composed of at least one kind of vegetable wax having a

melting point based on the DSC method of from 66°C to 86°C or at least one kind of polyethylene based wax having a melting point based on the DSC method of from 80°C to 140°C, wherein when the dynamic friction coefficient of a toner base is represented as BF, the dynamic friction coefficient of the external additive is represented as GF, the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to the toner base is represented as TF, the BET specific surface area of the toner base is represented as SB, and the BET specific surface area of the toner after performing the external addition treatment is represented as ST, BF is from 0.10 to 0.25, GF is from 0.12 to 0.30, and both the relationships represented by the general formulae (Mathematical expression 1) and (Mathematical expression 2) are satisfied.

[0056] As the first configuration of the carrier according to the present invention, a carrier is provided which is a magnetic material having a surface coated with a resin containing an electrically conductive fine powder and which is characterized in that the surface of the coated resin film has a contact angle of from 90 to 120 degrees.

[0057] As the second configuration of the carrier according to the present invention, a carrier is provided which is a magnetic material having a surface coated with a resin containing an electrically conductive fine powder and which

is characterized in that the dynamic friction coefficient between the coated resin film and a steel ball is from 0.01 to 0.1.

[0058] As the third configuration of the carrier according to the present invention, a carrier is provided which is a magnetic material having a surface coated with a resin containing an electrically conductive fine powder and which is characterized in that the dynamic friction coefficient between the coated resin film and a toner according to any one of Claims 1 to 8 is from 0.1 to 0.3.

[0059] As the configuration of the two-component developer according to the present invention, a two-component developer is provided which is characterized in that the charge rising index in the mixing of a carrier and a toner is 0.6 to 1.3.

[0060] In the toner according to any one of the first, second, third, fourth, fifth, sixth, seventh, and eighth configurations of the present invention, preferably, the external additive to be added to the toner is composed of at least one of silicon oxide fine powders, titanium oxide fine powders, magnetite fine powders, titanate fine powders, zirconia acid salt fine powders, and tungsten carbide fine powders.

[0061] In the toner according to any one of the first, second, third, fourth, fifth, sixth, seventh, and eighth

configurations of the present invention, preferably, the vegetable wax to be added to the toner is at least one member selected from the group consisting of carnauba waxes having a melting point based on the DSC method of from 80°C to 86°C, candelilla waxes having that of from 68°C to 72°C, hydrogenated jojoba oils having that of from 66°C to 72°C, and rice waxes having that of from 79°C to 83°C.

[0062] In the toner according to any one of the first, second, third, fourth, fifth, sixth, seventh, and eighth configurations of the present invention, preferably, the polyethylene based wax to be added to the toner is produced by a pyrolysis method has a recovery rate of 95% or more when being washed with toluene at 25°C for 1 hour.

[0063] In the toner according to any one of the first, second, third, fourth, fifth, sixth, seventh, and eighth configurations of the present invention, preferably, the binder resin serving as a main component of the toner is a styrene (meth)acrylic acid alkyl ester copolymer having a weight average molecular weight Mw of from 100,000 to 500,000, a ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn of from 40 to 90, a ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn of from 350 to 900, and a 1/2 outflow temperature measured by Koka type flow tester of from 105°C to 145°C.

[0064] In the toner according to any one of the first, second, third, fourth, fifth, sixth, seventh, and eighth configurations of the present invention, preferably, the binder resin serving as a main component of the toner is a polyester resin having a weight average molecular weight Mw of from 10,000 to 300,000, a ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn of from 3 to 50, a ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn of from 10 to 800, a 1/2 outflow temperature measured by Koka type flow tester of from 80°C to 150°C, and a flowing start temperature of 80°C to 120°C and being produced by polycondensation of polyvalent carboxylic acid or lower alkyl ester thereof with polyhydric alcohol.

[0065] In the carrier according to any one of the first, second, and third configurations of the present invention, preferably, the resin constituting the coated layer of the carrier is a resin composed of at least one member selected from the group consisting of silicone resins and acrylic resins.

[0066] In the carrier according to any one of the first, second, and third configurations of the present invention, preferably, the resin constituting the coated layer of the carrier is composed of at least a resin formed from an alkyl (meth)acrylate polymer including a long alkyl chain having

from 14 to 26 carbon atoms.

[0067] The toner, carrier, or two-component developer according to any one of the above-described configurations of the present invention is suitable for use in an electrophotographic method including a waste toner recycle step of recovering the toner remaining on an image bearer after a transfer process to be reused for a developing process in a developing apparatus.

[0068] The toner, carrier, or two-component developer according to any one of the above-described configurations of the present invention is suitable for use in an electrophotographic method including a toner transfer step of transferring a toner image, which is formed on an image bearer by converting an electrostatic latent image to a visual image, to a transfer material inserted between the image bearer and an electrically conductive elastic roller while applying a transfer bias voltage to the electrically conductive elastic roller.

[0069] The toner, carrier, or two-component developer according to any one of the above-described configurations of the present invention is suitable for use in an electrophotographic method including a transfer system in which a primary transfer process for transferring a toner image, which is a visualized image of an electrostatic latent image formed on the image bearer, to a surface of an

endless intermediate transfer member by bringing the surface of the endless intermediate transfer member into contact with the image bearer is repeatedly performed a plurality of times, and then a secondary transfer process is performed to collectively transfer the superimposed toner images, which are formed on the surface of the intermediate transfer member by repeatedly performing the primary transfer process a plurality of times, to a transfer member.

[0070] The toner, carrier, or two-component developer according to any one of the above-described configurations of the present invention is suitable for use in a color electrophotographic apparatus including a plurality of movable image formation units having at least respective rotating image bearers and developing devices with different colors toners to form mutually different color toner images on the respective image bearers; an image formation position composed of a single exposure position and a single transfer position; an image formation unit group in which the plurality of image formation units are placed annularly; a movement device for rotationally moving the entire image formation unit group to sequentially move the individual image formation units to the single image formation position; a light irradiating device for emitting signal light; and a mirror which is located at substantially the center of rotation of the rotational movement of the above-

described image formation unit group for guiding the light from the light irradiating device to the exposure position, wherein a color image is formed by transferring the different color toner images to a transfer material while the toner images are registered and superimposed.

[0071] A binder resin having a wide molecular weight distribution is used in order to respond to a wide range of developing process speeds and, in addition, a polyethylene wax or a vegetable wax having specific properties is added in order to increase the penetrability into the paper and to allow the fixed image surface to achieve a low friction state, so that a good fixing property can be obtained. Furthermore, proper materials and manufacturing conditions are chosen and set in such a way that the dynamic friction coefficient of the external additive to be added to the toner, the dynamic friction coefficient of the toner base before performing the external addition treatment, the dynamic friction coefficient of the toner after performing the external addition treatment, the BET specific surface area of the toner base before performing the external addition treatment, and the BET specific surface area of the toner after performing the external addition treatment satisfy the specific relationships. Therefore, the blade-cleaning property is made excellent while the fixing property and the offset resistance are satisfied, and

foreign matters, that is, low resistance substances on the photoreceptor, can be removed effectively. The friction coefficient and the contact angle of the coating film of the carrier are specified and, thereby, in the two-component developing, the mixing property of the carrier with the toner is made uniform to improve the electrostatic charge property. In particular, occurrence of background fogging due to delay in electrostatic charging when the toner is rapidly replenished can be prevented. Furthermore, it has been found that a toner having an excellent waste toner recycling property and an excellent transfer property in transferring using a transfer roller or intermediate transferring has been obtained.

[0072]

[Embodiments] In the present invention, the binder resin is a styrene (meth)acrylic acid alkyl ester copolymer and includes at least a polymer produced by copolymerizing a styrene based monomer. In the above description, "(meth)acryl···" refers to "acryl···" or "methacryl···".

[0073] Specific examples of styrene based monomers can include styrene; substitution products of styrene, e.g., α-methyl styrene and P-chlorostyrene; acrylic acid; acrylic acid alkyl ester, e.g., methyl acrylate, ethyl acrylate, butyl acrylate, dodecyl acrylate, octyl acrylate, isobutyl acrylate, and hexyl acrylate; methacrylic acid; methacrylic

acid alkyl esters, e.g., methyl methacrylate, ethyl methacrylate, butyl methacrylate, octyl methacrylate, isobutyl methacrylate, dodecyl methacrylate, and hexyl methacrylate. Known polymerization methods, e.g., bulk polymerization, solution polymerization, suspension polymerization, and emulsion polymerization, can be used as the method for manufacturing the polymer. In the present invention, a polymer produced by polymerizing the above-described vinyl monomer is used as a primary component of the binder resin. If necessary, a polymer, e.g., a polyester resin, an epoxy resin, or a polyurethane resin, other than the polymer produced by polymerizing the vinyl monomer, can be contained in the binder resin.

[0074] In the present invention, in order that the toner can be used in a wide range of developing process speeds (from 140 mm/sec to 480 mm/sec), it is necessary that not only the fixing property and the electrostatic charge property of the toner are improved by improving the dispersibility of the additive in the above-described kneading process, but also the penetration force of the binder resin into the paper by heat-melting is further increased; the slippiness of the surface of the toner fixing image is increased; and appropriate viscoelasticity is imparted in order to improve the offset resistance of the toner. It is preferable that the composition, the glass

transition point, and the molecular weight of each of the low-molecular weight polymer component and the high-molecular weight polymer component of the binder resin are specified in order to increase the penetration force into paper and improve the offset resistance.

[0075] Specifically, it is preferable that the binder resin contains a styrene based polymer having a weight average molecular weight within the range of from 2,500 to 20,000 and a glass transition point of from 50°C or higher as the low-molecular weight polymer component and contains a styrene-acryl copolymer having a weight average molecular weight of 100,000 or more, a glass transition point within the range of from 50°C to 70°C, preferably a weight average molecular weight of 120,000 or more and a glass transition point within the range of from 55°C to 70°C, and more preferably a weight average molecular weight of 150,000 or more and a glass transition point within the range of from 55°C to 65°C as the high-molecular weight polymer component. Preferably, the blending ratio of the low-molecular weight polymer component to the high-molecular weight polymer component is within the range of from 9:1 to 5:5. For the entire binder resin, preferably, the weight average molecular weight Mw is from 100,000 to 500,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 40 to 90, the

ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 350 to 900, and the 1/2 outflow temperature (hereafter referred to as a softening point) measured by Koka type flow tester is from 105°C to 145°C.

[0076] It is more preferable that the weight average molecular weight Mw is from 120,000 to 450,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 45 to 85, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 400 to 800, and the softening point is from 110°C to 140°C. It is further preferable the weight average molecular weight Mw is from 120,000 to 350,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 55 to 85, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 400 to 700, and the softening point is from 115°C to 140°C.

[0077] Preferably, the binder resin contains 50 to 95 percent by weight of styrene based components in order to further improve the fixing property and the pulverization property during the pulverization in the manufacturing stage. The flowing start temperature of the binder resin measured by a flow tester is within the range of from 80°C to 120°C,

preferably within the range of from 85°C to 110°C, and more preferably within the range of from 95°C to 108°C.

[0078] In the case where the toner of the present invention is used as a color toner, a polyester resin can be suitable for use as the binder resin.

[0079] The binder resin is composed of a polyester resin produced by polycondensation of polyvalent carboxylic acid or lower alkyl ester thereof with polyhydric alcohol. Examples of polyvalent carboxylic acid or lower alkyl ester can include aliphatic dibasic acids, e.g., malonic acid, succinic acid, glutaric acid, adipic acid, and hexahydrophthalic anhydride; aliphatic unsaturated dibasic acids, e.g., maleic acid, maleic anhydride, fumaric acid, itaconic acid, and citraconic acid; aromatic dibasic acids, e.g., phthalic anhydride, phthalic acid, terephthalic acid, and isophthalic acid; and methyl esters, ethyl esters, and the like thereof. Among them, aromatic dibasic acids, e.g., phthalic acid, terephthalic acid, and isophthalic acid and lower alkyl esters thereof are preferable.

[0080] Examples of polyhydric alcohol can include diols, e.g., ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butylene glycol, 1,4- butylene glycol, 1,6-hexane diol, neopentyl glycol, diethylene glycol, dipropylene glycol, bisphenol A ethylene oxide adducts, and bisphenol A propylene oxide adducts; triols, e.g., glycerin,

trimethylolpropane, and trimethylolethane; and mixtures thereof. Among them, neopentyl glycol, trimethylolpropane, bisphenol A ethylene oxide adducts, and bisphenol A propylene oxide adducts are preferable.

[0081] Known polycondensation, solution polycondensation, or the like can be used as the polymerization. In this manner, a satisfactory toner can be obtained without impairing the vinyl chloride mat resistance and the color of the coloring material of the color toner.

[0082] In general, the ratio of usage of the polyvalent carboxylic acid to the polyhydric alcohol is 0.8 to 1.4 usually in terms of the ratio (OH/COOH) of the number of hydroxyl groups to the number of carboxylic groups. Preferably, the hydroxyl value of the polyester resin is from 6 to 100.

[0083] For this polyester, preferably, the weight average molecular weight Mw is from 10,000 to 300,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 3 to 50, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 10 to 800, the 1/2 outflow temperature (hereafter referred to as a softening point) measured by Koka type flow tester is from 80°C to 150°C, and the flowing start temperature is within the range of from 80°C to 120°C.

[0084] From the view point of the light transmitting property and the gloss, the toner used in a color process in which an image of superimposed four colors is formed and fixed preferably has the following properties. Specifically, the weight average molecular weight Mw is from 10,000 to 180,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 3 to 20, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 10 to 300, the softening point is from 85°C to 120°C, and the flowing start temperature is within the range of from 80°C to 110°C. More preferably, the weight average molecular weight Mw is from 10,000 to 150,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 3 to 16, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 10 to 260, the softening point is from 90°C to 115°C, and the flowing start temperature is within the range of from 85°C to 110°C. Further preferably, the weight average molecular weight Mw is from 10,000 to 100,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 5 to 12, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 14 to 220, the softening point is from 95°C to 115°C, and the

flowing start temperature is within the range of from 85°C to 105°C.

[0085] In the case where the toner is used as a black toner in a black-and-white process in which developing is performed with a single color, there is no need to specifically take the light transmitting property and the smoothness into consideration. However, for example, in the case where the toner must be used in a wide range of developing process speeds (from 140 mm/sec to 480 mm/sec), it is necessary that not only the fixing property and the electrostatic charge property of the toner are improved by improving the dispersibility of the additive in the above-described kneading, but also the penetration force of the binder resin into paper by heat-melting is further increased, the slippiness of the surface of the toner fixing image is increased, and appropriate viscoelasticity is imparted in order to improve the offset resistance. Consequently, it is preferable that the weight average molecular weight Mw is from 50,000 to 300,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 5 to 50, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 50 to 800, the softening point is from 90°C to 150°C, and the flowing start temperature is within the range of from 80°C to 120°C. More preferably, the weight average

molecular weight Mw is from 80,000 to 250,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 7 to 45, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 100 to 700, the softening point is 95°C to 146°C, and the flowing start temperature is within the range of from 85°C to 115°C. Further preferably, the weight average molecular weight Mw is from 100,000 to 220,000, the ratio Mw/Mn of the weight average molecular weight Mw to the number average molecular weight Mn is from 9 to 45, the ratio Mz/Mn of the Z average molecular weight Mz to the number average molecular weight Mn is from 150 to 600, the softening point is from 100°C to 142°C, and the flowing start temperature is within the range of from 85°C to 110°C.

[0086] The weight average molecular weight of the above-described binder resin is a value measured by gel·permeation·chromatography in which several types of monodisperse polystyrene are used as standard samples. That is, a measurement value is obtained by flowing tetrahydrofuran serving as a solvent at a flow rate of 1 ml per minute at a temperature of 25°C and injecting a tetrahydrofuran sample solution having a concentration of 0.5 g/dl into the solvent by 10 mg in terms of a weight of sample. The measurement condition is set in such a way that

the molecular weight distribution of the object sample is included within the range in which the logarithm of the molecular weight and the number of counts are in a linear relationship on the calibration curve obtained by the several types of monodisperse polystyrene standard samples.

[0087] With respect to the softening point of the binder resin, a flow tester (CFT500) produced by SHIMADZU CORPORATION is used, and $1cm^3$ of sample is extruded from a nozzle having a diameter of 1 mm while heating is performed at a temperature rising rate of 6°C/min and a load of 20 kg/cm^2 is applied by a plunger. From the relationship between the amount of downward movement of this plunger and temperature rising characteristic, when the height of the characteristic line thereof is represented by h, the temperature corresponding to h/2 is the softening point.

[0088] When the binder resin, in which the composition, the glass transition point, and the molecular weight of each of the above-described low-molecular weight polymer component and the high-molecular weight polymer component are specified, is used, although the fixing strength evaluated by a tape peeling test of the toner fixing image is improved, if the toner fixing image surface is rubbed, the toner is easily peeled off from the transfer material. In the present invention, it is preferable that a vegetable wax having a low dynamic friction coefficient is contained in

the toner in order to improve the abrasion resistance of such the toner fixing image. In the present invention, a vegetable wax having a melting point based on the DSC method of 66°C to 86°C is preferable. This functions as a fixing improver, and exerts the effects of decreasing the friction resistance on the image surface, improving the fixing property and, in addition, improving the offset resistance. Preferably, the amount of addition is 1 to 20 parts by weight per 100 parts by weight of the binder resin.

[0089] It is preferable that the vegetable wax is a carnauba wax having a melting point based on the DSC method of from 80°C to 86°C and an acid value of 2 to 10, a candelilla wax having a melting point based on the DSC method of from 68°C to 72°C and an acid value of from 12 to 20, a hydrogenated jojoba oil having a melting point based on the DSC method of from 66°C to 72°C, an acid value of 3 or less, and a heating loss at 220°C of 2% or less, and a rice wax having a melting point based on the DSC method of from 79°C to 83°C and an acid value of from 2 to 13. These can be used alone or in combination of at least two types.

[0090] In the present invention, it is also preferable to add a polyethylene wax to the above-described binder resin. This functions as a fixing improver, and exerts the effects of decreasing the friction resistance on the image surface and improving the fixing property. A polyethylene wax

produced by a pyrolysis method is preferable. The recovery rate is 95% or more when washing is performed with toluene at 25°C for 1 hour. The melting point of the polyethylene wax based on the DSC method is from 80°C to 140°C, preferably from 90°C to 135°C, and more preferably within the range of from 95°C to 135°C. If the melting point is higher than 140°C, the releasing agent is not melted in fixing, the releasing agent does not melt into the interface between a fixing hard roller and the toner, high temperature offset tends to occur, the friction reduction effect is reduced, and the fixing property improvement effect is reduced. If the melting point is 80°C or less, the heat resistance of the toner is deteriorated, so that agglomeration and solidification tend to occur. In general, the wax is added by 0.1 to 20 parts by weight, preferably 1.0 to 15 parts by weight per 100 parts by weight of the binder resin.

[0091] In the present invention, it is more preferable that the polyethylene wax and the vegetable wax are used in combination.

[0092] In addition, examples of releasing agents include low-molecular weight polyalkylenes, e.g., low-molecular weight polypropylene, ethylenebisamide, montan wax, and paraffinic wax. These are used alone, or a mixture of at least two types is used. Preferably, these are in a form which is not compatible with the binder resin and which

tends to be liberated.

[0093] The addition of these low-friction waxes is preferable for the fixing property, the durability, and the like. However, when these are adhered to the photoreceptor, removal of low-resistance substances becomes difficult because of low friction, and image deletion will result at high humidities.

[0094] In contrast, in the present invention, mutual compatibility can be ensured because the external additive, the toner base, and the toner have dynamic friction coefficients within the specific ranges.

[0095] Preferably, a fine powder material having a dynamic friction coefficient of 0.12 to 0.30 is used as the external additive. A material having a dynamic friction coefficient of from 0.15 to 0.28 is more preferable, and a material having a dynamic friction coefficient of from 0.17 to 0.26 is further preferable. If the dynamic friction coefficient becomes 0.12 or less, low-resistance substances adhered to the photoreceptor surface cannot be removed effectively. Furthermore, since the mixing property with the carrier is too improved conversely, the charge rising edge property is deteriorated, and fog tends to occur temporarily, for example, when the toner is replenished. If the dynamic friction coefficient becomes 0.3 or more, not only a damage, e.g., a flaw, inflicted on the photoreceptor is increased,

but also curling tends to occur depending on the set condition of the cleaning blade. The mixing property with the carrier is deteriorated and the distribution of the amount of electrostatic charge becomes uneven.

[0096] In order to satisfy this coefficient, the external additives are used alone or in combination of at least two types. It is preferable that the fine powder material is hydrophobic silica fine particles composed of a silicon oxide fine powder, a titanium oxide fine powder, a magnetite fine powder, a titanate fine powder, or a zirconia acid salt fine powder. In particular, more preferably, hydrophobic silica and a fine powder thereof are used in combination in a mixture system.

[0097] The hydrophobic silica is silica fine particles produced by vapor phase oxidation of a silicic acid halogen compound and, for example, pyrolytic oxidation reaction of a silicon tetrachloride gas in an oxyhydrogen flame is used. For the use as a toner having a negative charge property, hydrophobic silica surface-treated with dimethyldichlorosilane, hexamethylenedisilazane, or polydimethylsiloxane is preferable. For the use as a toner having a positive charge property, hydrophobic silica surface-treated with aminosilane is preferable. It is preferable that the BET specific surface area of the above-described hydrophobic silica measured by nitrogen adsorption

is within the range of from 50 to 350 m^2/g. In general, the hydrophobic silica is blended by 0.1 to 5 parts by weight, preferably 0.2 to 3 parts by weight per 100 parts by weight of toner base particles.

[0098] Preferably, titanium oxide has a BET specific surface area of from 10 to 110 m^2/g and a degree of hydrophobicity of from 20 to 70. Preferably, the surface thereof is surface-treated with Al, silicone oil, a silane coupling agent, or the like.

[0099] Preferably, magnetite and the tungsten carbide fine particles are in the shape of a sphere, an octahedron, or a hexahedron. Preferably, the BET specific surface area is from 1.0 to 10.

[0100] Among the inorganic fine particles, the titanate fine powder and the zirconia acid salt fine powder are more suitable for use. Fine particles produced by a solid phase method, a fine particle synthesis method under the hydrothermal condition, an oxalate pyrolysis method, or the like are suitable for use.

[0101] For example, in the case where barium titanate fine particles are produced by the oxalate pyrolysis method, a mixed solution A (kept at 30°C or lower) of $TiCl_4$(aq) and $BaCl_2 \cdot 2H_2O$ is prepared, and the resulting mixed solution A is dropped into an oxalic acid $(COOH)_2 \cdot 2H_2O$ aqueous solution kept at 80°C, so that $BaTiO(C_2O_4) \cdot 4H_2O$ is produced. This is

heated to 600°C or more and, thereby fine particles of BaTiO3 are produced. Examples of the fine particle synthesis method under the hydrothermal condition include a hydrothermal oxidation method, a hydrothermal precipitation method, a hydrothermal synthesis method, a hydrothermal dispersion method, a hydrothermal crystallization method, a hydrothermal hydrolysis method, a hydrothermal attritor mixing method, and a hydrothermal mechanochemical method. The hydrothermal oxidation method, the hydrothermal precipitation method, the hydrothermal synthesis method, the hydrothermal dispersion method, and the hydrothermal hydrolysis method are preferable.

[0102] Examples of materials synthesized by the hydrothermal method include $CaSiO_3$, $LaCrO_3$, $AlPO_4$, NbP_3O_4, $LaFeO_3$, $LiNbO_3$, $SrTiO_3$, $BaTiO_3$, $CaTiO_3$, $PbTiO_3$, $FeTiO_3$, $SrZrO_3$, $BaZrO_3$, $CaZrO_3$, $PbZrO_3$, $MnSiO_3$, $MgSiO_3$, MoO_2, SnO_2, ZnO_2, MgO_2, NiO, V_2O_5, $Nb2O_5$, WO_2, Nb_2O_3-TiO_2, Ta_2O_5-TiO_2, and V_2O_5-ZnO_2. Preferably, $SrTiO_3$, $BaTiO_3$, $MgTiO_3$, $AlTiO_3$, $CaTiO_3$, $PbTiO_3$, $FeTiO_3$, $SrZrO_3$, $BaZrO_3$, $MgZrO_3$, $AlZrO_3$, $CaZrO_3$, $PbZrO_3$, $MnSiO_3$, $CaSiO_3$, and $MgSiO_3$ are included. More preferably, titanates, e.g., $SrTiO_3$, $BaTiO_3$, $MgTiO_3$, $AlTiO_3$, $CaTiO_3$, $PbTiO_3$, and $FeTiO_3$, and zirconates, e.g., $SrZrO_3$, $BaZrO_3$, $MgZrO_3$, $AlZrO_3$, $CaZrO_3$, and $PbZrO_3$, are included.

[0103] Inorganic materials, e.g., titanates and zirconate fine particles, are electrostatically charged with a

polarity opposite to the polarity of the organic material of the above-described magnetic toner binder resin of the present invention. Furthermore, for example, with respect to the positive charge property, a high positive charge property can be obtained by a titanium coupling agent, a surface treatment of a coupling agent having a nitrogen group or an organic material having a nitrogen group, or the like. At this time, the average particle diameter is from 0.05 to 4 μm and the BET specific surface area measured by nitrogen adsorption is from 0.1 to 40 m^2/g, preferably, the average particle diameter is from 0.1 to 3 μm and the BET specific surface area measured by nitrogen adsorption is from 1.0 to 20 m^2/g, and more preferably, the average particle diameter is from 0.5 to 2 μm and the BET specific surface area measured by nitrogen adsorption is 2 to 15 m^2/g. In addition, inorganic fine particles having a static bulk density of from 0.2 to 1.2 g/cm^3 is used, furthermore, inorganic fine particles having a true specific gravity of from 5.0 to 8.5 g/cm^3 are used and, thereby, the dispersibility of the inorganic fine particles is further improved, the adhesion to the base particles of the magnetic toner is made uniform, and an effect is exerted on prevention of filming.

[0104] If the average particle diameter becomes 0.05 μm or less, the dispersibility of the inorganic fine particles is

deteriorated, the agglomerate is increased, and an image defect results. If the BET specific surface area measured by nitrogen adsorption becomes 40 m^2/g or more, the dispersibility of the inorganic fine particles is deteriorated likewise, the agglomerate is increased, and an image defect results. If the static bulk density becomes 0.2 g/cm^3 or less, the agglomeration property of the inorganic fine particles is enhanced and, thereby, the dispersibility is deteriorated.

[0105] If the average particle diameter becomes 4 μm or more, liberation from the magnetic toner base particles occur, and an unwanted flaw is inflicted on the photoreceptor. If the BET specific surface area measured by nitrogen adsorption becomes 0.1 m^2/g or less, coarse particles are increased, liberation from the magnetic toner base particles occur, and an unwanted flaw is inflicted on the photoreceptor.

[0106] Fine particles synthesized by this method become spherical fine particles exhibiting reduced agglomeration, narrow particle size distribution, and good fluidity. Consequently, when the fine particles are subjected to an external addition treatment to the toner, good dispersibility is exhibited and adhesion to the toner is uniform. Since the shape is spherical, an unwanted flaw is not inflicted on the photoreceptor.

[0107] Preferably, the amount of addition of the inorganic fine particles is from 0.1 to 5.0 parts by weight relative to 100 parts by weight of the magnetic toner. If the amount is 0.1 parts by weight or less, an effect of preventing the filming is at a low level, and if the amount is 5.0 parts by weight or more, the agglomeration property is enhanced and, thereby, an unwanted flaw is inflicted on the photoreceptor.

[0108] It is preferable that the toner of the present invention has a dynamic friction coefficient of from 0.15 to 0.35.

[0109] In the present invention, when the dynamic friction coefficient of the external additive is represented as GF and the dynamic friction coefficient of the toner after performing an external addition treatment to add the external additive to a toner base is represented as TF, it is preferable that a relationship represented by the general formula (Mathematical expression 1) is satisfied.

[0110] When a toner exhibiting a reverse tendency is used, it is difficult to remove low-resistance substances on the photoreceptor. When a waste toner is recycled, a phenomenon occurred in which fog was increased. Furthermore, in the toner of the present invention, when the dynamic friction coefficient of a toner base pulverized, classified, and before performing an external addition treatment is represented as BF, it is preferable that a relationship

represented by the general formula (Mathematical expression 2) is satisfied.

[0111] If this tendency is not followed, it is difficult to remove low-resistance substances on the photoreceptor, and when a waste toner is recycled, fog is increased. When BF was further increased, the frequency of occurrence of phenomenon, in which pealing was readily caused by a cleaning blade, was increased. The factor is not clear, but it is believed that the state of adhesion of the additive in the external addition treatment is influenced by the slippiness of the surface of the toner base and the detaching property of the additive from the toner surface subjected to external addition treatment.

[0112] In the present invention, when the BET specific surface area of the toner base is represented as SB and the BET specific surface area of the toner after performing the external addition treatment of the additive is represented as ST, it is preferable that the external addition treatment condition is set to satisfy the relationship represented by a general formula (Mathematical expression 3).

[0113] That is, an external additive having a large specific surface area must be treated in such a way that a part thereof is embedded in the toner base with some extent of strength. An external additive having a small specific surface area is in no need of being subjected to the

external addition treatment to the toner base with the same extent of strength as that of the material having a large specific surface area. The external addition treatment is influenced by a blade shape of a mixer, the number of revolutions, time, temperature in a vessel, the amount of input, and furthermore, a toner material to be used. If the ST/SB becomes less than 1.1, the external additive implanted strongly in the toner base surface is increased, the friction coefficient of the toner is reduced, the cleaning property is deteriorated, the effect of removing foreign matters of the photoreceptor is deteriorated, and the electrostatic charge property and the fluidity of the toner itself are also deteriorated. If the ST/SB exceeds 6, silica fine particles and the like having particularly large specific surface area are liberated from the toner frequently, and thereby, implantation and the like into the photoreceptor and the like occur, so that a black stripe or a white stripe results.

[0114] The BET specific surface area was measured with FlowSorbII2300 produced by SHIMADZU CORPORATION.

[0115] The dynamic friction coefficient was measured with HEIDON Type 14 Friction coefficient measuring apparatus.

[0116] The toner to be measured was applied uniformly to a glass präparat surface on a stage by using a blade so as to form a thin layer. A cover glass was attached to an

indenter attachment portion of the apparatus, the stage was moved while the toner layer was held between the glass präparat and the cover glass, and the friction coefficient at that time was measured with a load converter. However, when this method is performed, since the toner thin layer is not produced constantly, large variations in friction coefficient value occur in the measurement, and the data tend to lack stability. Therefore, the following method was adopted.

[0117] A predetermined load was applied while the toner layer was held between the glass präparat and the cover glass, and the stage was allowed to reciprocate a predetermined times.

[0118] Subsequently, the glass präparat and the cover glass were temporarily detached from the apparatus, and were attached again to the apparatus after the adhered toner was removed lightly with air.

[0119] The stage was moved while the glass präparat and the cover glass were in contact with each other. The friction coefficient at that time was measured with a load converter and was taken as the dynamic friction coefficient.

[0120] In the electrophotographic method, the toner remaining after the transfer is in the state of being rubbed against the photoreceptor surface with the cleaning blade, the low-melting point wax and the like added to the toner

remain on the photoreceptor so as to cause filming, and it becomes difficult to remove low-resistance substances because the slippiness of the photoreceptor surface is improved. It is believed that the present method for measuring a friction coefficient is suitable for evaluation in the form close to this state. The friction coefficient varies depending on the slippiness, the amount of adhesion, and the like of the toner constituent materials adhering and remaining on the surfaces of the glass präparat and the cover glass. In order to correlate with the actual apparatus, when the correlation to the amounts of shaving of the films of the photoreceptor after a durability test of a predetermined number of films was examined, good reproducibility was ascertained.

[0121] In the present invention, known materials can be used as a charge controlling agent. For the positive charge material, an azine based compound is preferable. It is preferable that the amount of addition is from 0.1 to 5 parts by weight relative to 100 parts by weight of binder resin. Furthermore, other appropriate pigment or dye is blended with the binder resin for the purpose of coloring and/or charge control of the toner. Examples of such pigment or dye can include carbon black, iron black, graphite, a metal complex of azo dye with Cr, Ni, or the like, aniline blue, phthalocyanine blue, phthalocyanine blue,

Hansa yellow G, rhodamine 6C lake, Calco Oil Blue, chrome yellow, quinacridone, benzidine yellow, rose Bengal, DuPont Oil Red, and triallylmethane based dyes. At least one type of them is used alone or as a mixture. An amount required for coloring and/or charge control is added to the binder resin.

[0122] In the present invention, if necessary, a magnetic powder can be added to the binder resin. Examples thereof include metal powders of iron, manganese, nickel, and cobalt and ferrites of iron, manganese, nickel, cobalt, and zinc. In general, the average particle diameter of the powder is 1 μm or less, preferably 0.6 μm or less. The magnetic powder is added by 15 to 70 percent by weight relative to the entire toner. If the amount of addition is 15 percent by weight or less, there is a tendency of scattering of the toner to increase, and if the amount is 70 percent by weight or more, the amount of electrostatic charge of the toner is decreased, and there is a tendency of deterioration of the image quality to result.

[0123] In the manufacturing process of the toner, basically, a pre-mixing treatment of various materials, a melting and kneading treatment, a pulverization and classification treatment, and an external addition treatment are performed in that order.

[0124] The pre-mixing treatment is a treatment in which the

binder resin and the additive to be dispersed therein are uniformly dispersed with, for example, a mixer provided with an agitation blade. A known mixer, e.g., Super Mixer (produced by Kawata Corporation), Henschel Mixer (produced by Mitsui Miike Kogyo), PS Mixer (produced by Shinko Pan Tech Co., Ltd.), or Loedige Mixer, is used as the mixer.

[0125] The melting and kneading treatment is a treatment in which the additive is dispersed into the binder resin by a shearing force, and is performed by Twin screw extruder (produced by Ikegai Ltd.) of a partitioned segment system including a cylinder and a kneading shaft which are partitioned into a plurality of segments.

[0126] In the pulverization and classification treatment, a toner mass produced by a kneading treatment and cooling is coarsely crushed with a cutter mill or the like and, thereafter, is finely pulverized by jet mill pulverization (for example, IDS pulverizer produced by Nippon Pneumatic Manufacturing Co., Ltd.) or the like. If necessary, fine powder particles are cut by an air stream classifier, so that toner particles (toner base particles) having a predetermined particle size distribution are produced. The pulverization and the classification can also be performed mechanically. For example, Criptron pulverizer (produced by Kawasaki Heavy Industries, Ltd.), in which the toner is put into a fine gap between a fixed stator and a roller rotating

relative to the stator and is pulverized, Turbo mill (produced by TURBO KOGYO CO., LTD.), or the like is used therefor. By this classification treatment, toner particles (toner base particles) having a volume average particle diameter generally within the range of 5 to 12 μm, preferably within the range of 5 to 9 μm are produced.

[0127] The external addition treatment is a treatment in which an external additive, e.g., silica, is mixed to the toner particles (toner base particles) produced by the above-described classification. A known mixer, e.g., Henschel Mixer or Super Mixer, is used therefor.

[0128] The toner of the present invention is suitable for use in single-component developing as well as two-component developing.

[0129] In the use for the two-component system, preferably, the carrier is a magnetic material coated with a resin containing an electrically conductive fine powder. Examples of electrically conductive fine powders to be used include metal powders, carbon black, semiconductive oxides, e.g., titanium oxide and zinc oxide, those in which the surfaces of the powders of titanium oxide, zinc oxide, barium sulfate, aluminum borate, potassium titanate, and the like are coated with tin oxide, carbon black, and metals. Preferably, the intrinsic resistance thereof is 1,010 Ω·cm or less.

[0130] For a core material of the carrier, nonmetals,

metals, and metal alloys, e.g., cobalt, iron, copper, nickel, zinc, aluminum, brass, and glass, which have been used previously and have an average particle diameter of from 20 to 100 μm, preferably from 30 to 80 μm, are used widely.

[0131] Examples of methods for forming a coating layer on the core material of the carrier include known coating methods, e.g., a dipping method in which a powder serving as a carrier core material is dipped in a solution for forming a coating layer, a spraying method in which a solution for forming a coating layer is sprayed on a surface of the carrier core material, a fluidized bed method in which a solution for forming a coating layer is sprayed while the carrier core material is floated by fluidizing air, and a kneader coater method in which the carrier core material and a solution for forming a coating layer are mixed in a kneader coater and a solvent is removed.

[0132] Examples of resins to be used as coating layers of the carrier include straight silicone resins including an organosiloxane bond and modified products thereof, e.g., alkyd-modified, epoxy-modified, and urethane-modified products, fluororesins, styrene resins, acrylic resins, methacrylic resins, polyester resins, polyamide resins, epoxy resins, polyether resins, and phenol resins. These can be used alone or in combination. Furthermore, copolymers thereof can be used.

[0133] Preferably, the silicone resin is a room temperature curing silicone resin. Examples thereof include KR271, KR255, KR152 (produced by Shin-Etsu Chemical Co., Ltd.), SR2400, SR2406, and SH840 (produced by Toray Silicone Co., Ltd.).

[0134] In the present invention, preferably, the contact angle of the film coated on the surface of the carrier is within the range of from 90 to 120 degrees. More preferably, the surface contact angle is from 95 to 115 degrees, and from 100 to 115 degrees is further preferable.

[0135] If the contact angle becomes 90 degrees or lower, the low-melting point component of the toner tends to adhere, and the carrier is deteriorated remarkably. If the contact angle becomes 120 degrees or more, the uniformity of the surface is too increased, the amount of electrostatic charge becomes resistant to increase, and the charge rising edge property is deteriorated. The friction coefficient of the surface is reduced, and the slippiness against the toner becomes too good, so that there is a tendency of the charge rising edge property to be deteriorated conversely. Particularly, in the configuration in which the waste toner is recycled, the waste toner, which is returned to the developing machine, contains a high proportion of those exhibiting poor electrostatic charge property. Consequently, the charge rising edge property is particularly deteriorated

and an increase in fog results.

[0136] Furthermore, it is preferable that the dynamic friction coefficient between the resin coating film of the carrier and a steel ball is within the range of from 0.01 to 0.1. More preferably, the dynamic friction coefficient is from 0.01 to 0.08, and from 0.02 to 0.07 is further preferable.

[0137] It is preferable that the dynamic friction coefficient between the resin coating film of the carrier and the toner of the present invention is within the range of from 0.1 to 0.3. More preferably, the dynamic friction coefficient is from 0.1 to 0.27, and from 0.1 to 0.24 is further preferable.

[0138] If the dynamic friction coefficient relative to the steel ball is 0.01 or less and the dynamic friction coefficient relative to the toner of the present invention is 0.1 or less, the friction coefficient of the carrier surface is reduced, and the slippiness against the toner becomes too good, so that there is a tendency of the charge rising edge property to be deteriorated conversely. Particularly, in the configuration in which the waste toner is recycled, the waste toner, which is returned to the developing machine, contains a high proportion of those exhibiting poor electrostatic charge property. Consequently, the charge rising property is particularly deteriorated and

an increase in fog results.

[0139] If the dynamic friction coefficient relative to the steel ball is 0.1 or more and the dynamic friction coefficient relative to the toner of the present invention is 0.3 or more, it is believed that the degree of contact with the toner is reduced in the mixing with the toner and, thereby, variations occur in electrostatic charge.

[0140] Furthermore, it is preferable that the charge rising index in the mixing and agitation of the developer, in which the carrier and the toner is mixed, is from 0.6 to 1.3. More preferably, the index is from 0.7 to 1.2, and from 0.8 to 1.1 is further preferable. If the charge rising index becomes 0.6 or less, the amount of electrostatic charge is significantly reduced during a long period of continuous use, a fine line is thickened and resolution is reduced. If the charge rising index becomes 1.3 or more, the charge rising edge property of the toner is deteriorated, and fog and toner scattering occur.

[0141] Here, the charge rising index is defined as follows. In the mixing time with the carrier, when the value of the amount of electrostatic charge at a mixing time of 1 minute determined by a blowoff method is represented as QM1 and the value of the amount of electrostatic charge at a mixing time of 60 minute determined by a blowoff method is represented as QM60, the value of QM60/QMn1 is defined as the charge

rising index. A larger value indicates that there is a tendency of the electrostatic charge to increase gradually by mixing, and a smaller value indicates that the electrostatic charge is decreased by mixing. It is believed that in the two-component developing, when a fresh toner is replenished, the difference in electrostatic charge between the fresh toner and the toner present in the developing machine is increased, the electrostatic charge gets out of balance and, thereby background fog or scattering tends to occur. A toner was mixed with a carrier at a toner concentration of 3%, 100 g of the resulting mixture was put into a 100-ml polyethylene container, and agitation was performed at the number of revolutions of 100 rpm. The blowoff method was performed at an amount of developer of 0.3 g and an air pressure of 0.2 kg/cm^2 for a blow time of 90 sec.

[0142] It is difficult for a resin coating material to achieve the above-described contact angle of the resin coating film of the carrier, the dynamic friction coefficient, and the electrostatic charge index by a single substance alone. A mixture system of a plurality of coating agents or a copolymer system is required. Moreover, the film thickness and coating film formation conditions, e.g., a curing temperature and a time after the coating film is applied, exert influences.

[0143] For a preferable composition of the materials, in particular, a mixture system of a straight silicone resin, in which a side chain group is simply an alkyl group, e.g., a methyl group, having the carbon number of 1 to 4, a straight silicone resin having a side chain group containing a phenyl group, and a (meth)acrylic resin. Preferable examples of (meth)acrylic resins include (meth)acrylic acid alkyl ester polymer resins of (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, dodecyl (meth)acrylate, octyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and the like. Furthermore, the properties are more improved by including a resin, as a coating layer, composed of an alkyl (meth)acrylate polymer including a long alkyl chain which is represented by (Chemical formula 1) and which has from 14 to 26 carbon atoms.

[0144] The developing property, the fixing property, the waste toner recycling property are allowed to become better by using, in combination, the carrier coated with the above-described coating resin and having specific contact angle, dynamic friction coefficient, and electrostatic charge index and the toner including the material containing the vegetable wax or the like and having the specific dynamic friction coefficient.

[0145] The toner of the present invention is suitable for

use in an electrophotographic apparatus provided with a transfer system in which a transfer material is inserted between an image bearer and an electrically conductive elastic roller, and a transfer bias voltage is applied to the above-described electrically conductive elastic roller, so that an toner image on the above-described image bearer is transferred to the transfer material by using an electrostatic force. This is for the reason as described below. The above-described transfer system is based on contact transfer. Therefore, a mechanical force other than the electrical force acts on the transfer. Consequently, a toner with a reverse polarity and adhered to a photoreceptor surface may be transferred, although the toner should not be transferred essentially, or back pollution of the transfer paper may occur because the toner adhered to the photoreceptor surface may pollute the transfer roller surface when the transfer paper is not passed through. However, in the case where the above-described toner is applied to an image formation apparatus provided with the above-described toner transfer system, the fluidity of the toner is satisfactorily maintained and a toner with a reverse polarity is not generated, the filming of the toner or a low-softening point wax liberated from the toner on the photoreceptor surface can be prevented, so that pollution of the transfer paper by unnecessary toner particles can be

prevented. In addition, since the filming of the toner or a liberated low-softening point wax on the transfer roller surface can also be prevented, the image defect resulting from retransfer of the toner or the liberated low-softening point wax from the transfer roller surface to the photoreceptor surface can also be prevented.

[0146] The toner of the present invention is suitable for use in an electrophotographic apparatus provided with a waste toner recycle system in which the toner remaining on an image bearer after a transfer process is recovered into a developing apparatus and is reused in a developing process. Falling out of the additive is at a low level even when a mechanical impact is given to the toner of the present invention in the inside of a cleaning unit, a transport pipe connecting the cleaning unit to a developing unit, and the developing unit while the toner of the present invention is recovered from the cleaning unit to the developing unit. Generation of poorly charged toner (particles) recycled into the developing unit can be reduced, and reduction in the fluidity and the amount of electrostatic charge of the toner and the toner filming on the photoreceptor can be prevented in the waste toner recycle. Furthermore, reduction in the amount of electrostatic charge can be prevented during long period of continuous recycle use, and thickening of a fine line and reduction in resolution can be prevented. The

reason for this is believed that the charge rising edge property of the toner is good, and adhesion of foreign matters to the photoreceptor is suppressed.

[0147] The toner of the present invention is suitable for use in an electrophotographic apparatus provided with a transfer system configured in such a way that a primary transfer process to transfer a toner image formed on the above-described image bearer surface to a surface of an intermediate transfer member by bringing the surface of the endless intermediate transfer member into contact with the image bearer surface is repeatedly performed a plurality of times and, thereafter, a secondary transfer process is performed to collectively transfer superimposed toner images, which are formed on the above-described surface of the intermediate transfer member by repeatedly performing the primary transfer process a plurality of times, to a transfer member.

[0148] This is for the reason as described below. In the toner of the present invention, the additive is uniformly and homogeneously dispersed in the binder resin. Therefore, the low-melting point releasing agent does not fall out from the toner so as to cause filming on the intermediate transfer member, and reduction in transfer efficiency is suppressed. Since the friction property of the toner and the adhesion state of the external additive are set at an

appropriate state, the mutual adhesion of the toner particles is reduced, the agglomeration of the toner is loosened and, thereby a "hollow defect" phenomenon, in which a part of an image is not transferred due to agglomeration effect of the toner so as to form a hollow, can be reduced.

[0149] The toner of the present invention is suitable for use in a color electrophotographic apparatus including an image formation unit group in which a plurality of movable image formation units are placed annularly, the plurality of image formation units having their respective rotating photoreceptors and developing devices with toners of mutually different colors to form their respective toner images of mutually different colors on the above-described photoreceptors, wherein the entire image formation unit group is rotationally moved and a color image is formed by transferring the toner images, formed on the photoreceptors, of different colors to a transfer material while the toner images are registered and superimposed. Since the whole of the image formation units is configured to rotate, the situation in which the waste toner that has been cleaned from the photoreceptor and has been detached from the photoreceptor temporarily and repeatedly adheres again to the photoreceptor surely occurs. For the toner in which a low-melting point material, e.g., wax, is in a poor dispersion state, a high proportion of toner, in which wax

is unevenly distributed, is present in the waste toner. The waste toner is brought into contact repeatedly with the photoreceptor, so that filming on the image bearer tends to occur significantly, and a reduction in the life of the photoreceptor results. Furthermore, the toner vigorously moves in a vertical direction by the rotation of the image formation unit and, thereby, the toner tends to fall from a seal portion. Consequently, the seal must be further enhanced in the seal portion, a fusion phenomenon occurs in the toner in which a low-melting point material, e.g., wax, is in a poor dispersion state, and a mass is generated, so that an image noise of a black stripe or a white stripe results. The situation in which the toner is detached from the developing roller temporarily occurs at all times. If the charge rising edge property is deteriorated at an early stage of the developing, background fog results.

[0150] However, when the toner of the present invention is used, an occurrence of filming on the photoreceptor is avoided. In addition, since the charge rising edge property is good, there is no occurrence of background fog at the early stage of the developing.

[0151] In the fixing of a full color image, since the toner of the present invention includes low-melting point polyester, the fixing is performed in the form of substantially complete melt even in a fixed image in which

toners of four colors are superimposed. Furthermore, since the wax is dispersed, even in oil-less fixing, satisfactory offset resistance can be obtained and a fixed image of a color with no muddiness is produced while the glossiness is not impaired.

[0152]

[Examples] The present invention will be described below in further detail with reference to examples. The present invention is not limited to them.

[0153] (Example 1) Each of external additive fine particles to be added to a toner used in the present Example by the external addition treatment and the dynamic friction coefficient thereof are shown in (Table 1).

[0154]

[Table 1]

Sample No.	Fine particle material	BET specific surface area (m^2/g)	Treatment agent or manufacturing method	Dynamic friction coefficient
G1	SiO_2	110	dichlorosilane	0.25
G2	↑	165	↑	0.24
G3	↑	230	↑	0.23
G4	↑	90	dimethylsiloxane	0.20
G5	↑	184	hexamethylenedisilazane	0.17
G6	↑	140	↑	0.19
G7	↑	35	↑	0.20
G8	$BaTiO_3$	2.6	oxalate heating method	0.23
G9	↑	5.04	hydrothermal synthesis method	0.22
G10	Fe_3O_4	7.2		0.26
G11	TiO_2	49.1		0.24
G12	↑	31.5	silicone oil	0.22
G13	↑	21.5	↑	0.21
G14	WC	2.0		0.21

[0155] In the measurement of the dynamic friction coefficient of a toner, the toner is applied uniformly to a glass plate surface on a stage by using a blade, so as to form a thin layer. A glass plate of 18 mm long and 18 mm wide is attached to an indenter attachment portion of the apparatus, a weight of 500 g is placed on a pan in an upper portion of the indenter, a stage is allowed to reciprocate 200 times with a scanning width of 30 mm at a rate of 500 mm/sec, while the toner layer is held between a glass präparat and a cover glass. Subsequently, the glass präparat and the cover glass are temporarily detached from the apparatus, and are attached again to the apparatus after the adhered toner is removed lightly with air. A weight of 10 g is placed on the pan in the upper portion of the

indenter, a load converter is connected, and the stage is moved at 10 mm/sec. A value indicated by the apparatus at that time was taken as the dynamic friction coefficient.

[0156] Thermal properties of styrene butyl acrylate copolymer of the binder resin used in the present Example are shown in (Table 2).

[0157]

[Table 2]

Binder resin	Tg	Mn	Mw	Mz	Mw/Mn	Mz/Mn	Tm	Ti
RS1	56	2800	190000	1630000	68	582	131	105
RS2	60	3100	210000	1840000	67	594	130	106

[0158] In Table 1, Tg represents a glass transition temperature, Mn represents a number average molecular weight, Mw represents a weight average molecular weight, Mz represents a Z average molecular weight, Tm and Ti represent a softening point determined by a flow tester and a flowing start temperature.

[0159] A wax used in the present Example and a melting point Twt based on the DSC method is shown in (Table 3).

[0160]

[Table 3]

Sample	Twt (°C)	Acid value	Material	
W1	81	5	carnauba wax	S.KATO & co.
W2	79	10	rice wax	NS CHEMICAL CO., LTD
W3	68	0.9	hydrogenated jojoba oil M-1	Mitsuba Trading Co., Ltd.
W4	128	1	polyethylene wax	LEL400P (produced by Sanyo Chemical Industries, Ltd.)
W5	105	1	polyethylene wax	NL500(produced by Mitsui Petrochemical Industries, Ltd.)

[0161] The formulation of a toner used in Example is shown in (Table 4).

[0162]

[Table 4]

Binder resin	styrene butyl acrylate copolymer RS1, RS2	100 parts by weight
Magnetic material	magnetite (EPT500 produced by TODA KOGYO CORP.)	50 parts by weight
Charge controlling agent	azo dye (S34 produced by Orient Chemical Industries, Ltd.)	2 parts by weight
Wax	W1, W2, W3, W4, W5	
Releasing agent	polypropylene (TP32 produced by Sanyo Chemical Industries, Ltd.)	3 parts by weight
External additive	G1 to G14	

[0163] Toner samples and materials used in Example and various properties are shown in (Table 5). In the external addition treatment, when an external additive composed of one type of material, e.g., silica, having a large specific surface area is used, as in toners A1 to A4, since the agglomeration property is strong, some extent of rotation strength and time are required. However, when a mixture with a material having a small specific surface area is used, as in toners A5 to A9, if the external addition treatment is performed under the same condition as in the above description, there is a tendency of the filming removal effect to be reduced. Therefore, it is effective that the treatment is performed in two stages. For the treatment condition of the toners A1 to A4, Henschel Mixer (produced by Mitsui Miike Kogyo) is used, and the blade shape of Z0 +

S0 is used. The operation is performed at the number of revolutions of 1,800 rpm for a time of 6 min, wherein the amount of input is 1.5 kg, and the temperature in the vessel is 38°C. For the treatment condition of A5, A6, and A9, Henschel Mixer (produced by Mitsui Miike Kogyo) is used, and the blade shape of Z0 + S0 is used. First, the external addition treatment of silica alone is performed at the number of revolutions of 1,800 rpm for a time of 4 min with the amount of input of 1 kg. Subsequently, the predetermined amount of material having a small specific surface area is put in and the operation is continued at the number of revolutions of 1,700 rpm for a time of 2 min. Alternatively, first, the external addition treatment of silica alone is performed at the number of revolutions of 1,700 rpm for a time of 4 min with the amount of input of 1.5 kg. Subsequently, the predetermined amount of material having a small specific surface area is put in and the operation is continued at the number of revolutions of 1,200 rpm for a time of 4 min. That is, the latter treatment is performed at the reduced number of revolutions or for a reduced treatment time. Consequently, the dynamic friction coefficient and the value of specific surface area of the toner and the charge rising index when mixed with the carrier can be adjusted to appropriate values.

[0164]

[Table 5]

Toner sample No.	Binder resin	Wax	Amount of addition of wax (parts by weight)	External additive	Amount of addition of external additive (parts by weight)	GF	BF	TF	ST/SB
A1	RS2	W1	6	G2	1	0.25	0.20	0.28	1.30
A2	↑	W2	↑	G3	1	0.23	0.21	0.30	1.33
A3	↑	W3	↑	G1	1	0.25	0.24	0.32	1.35
A4	RS1	W3/W4	3/2	G2	1	0.24	0.21	0.30	1.32
A5	↑	W3/W5	3/4	G2/G8	1/1	0.26	0.22	0.31	1.40
A6	↑	↑	↑	G2/G10	1/0.5	0.28	↑	0.31	1.38
A7	RS2	↑	↑	G1/G11	1/0.5	0.27	↑	0.35	1.39
A8	↑	↑	↑	G2/G12	1/1	0.24	↑	0.32	1.45
A9	↑	↑	↑	G2/G14	1/1.2	0.23	↑	0.28	1.39

[0165] Fig. 1 is a sectional view showing the configuration of an electrophotographic apparatus used in the present Example 1, wherein the developing system is a magnetic single-component developing system. In Fig. 1, reference numeral 201 denotes an organic photoreceptor having a configuration in which a charge generation layer and a charge transport layer are laminated sequentially on an aluminum conductive support. In the charge generation layer, τ type metal-free phthalocyanine (produced by TOYO INK MFG. CO., LTD.) serving as a charge generation substance is dispersed in a polyvinyl butyral resin (S-LEC BL-1 produced by Sekisui Chemical Co., Ltd.). The charge transport layer includes a polycarbonate resin (Z-20 produced by Mitsubishi Gas Chemical Company, Inc.) and 1,1-bis(P-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene (T-405 produced by Anan). Reference numeral 202 denotes a magnet fixed coaxially with the photoreceptor 201, reference numeral 203 denotes a corona electric charger for electrostatically charging the photoreceptor negatively, reference numeral 204 denotes a grid electrode for controlling the electrostatic charge potential of the photoreceptor, and reference numeral 205 denotes signal light.

[0166] Reference numeral 207 denotes a magnetic single-component toner, reference numeral 206 denotes a toner

hopper for supplying the magnetic single-component toner 207 to the surface of the photoreceptor 201, reference numeral 208 denotes a non-magnetic electrode roller disposed with a gap from the photoreceptor 201, reference numeral 209 denotes a magnet disposed in the inside of the electrode roller 208, reference numeral 210 denotes an alternating-current high voltage power supply for applying a voltage to the electrode roller 208, reference numeral 211 denotes a scraper formed from a polyester film for scraping a toner on the electrode roller, and reference numeral 212 denotes a damper for allowing the toner to flow smoothly in the toner hopper and preventing the toner from being pressed by the self weight thereof to cause blocking between the photoreceptor and the electrode roller. A developing apparatus for converting a latent image after exposure to a visible image is composed of them. Here, the electrode roller 208 is to recover an excess toner from a non-image portion.

[0167] Reference numeral 213 denotes a transfer roller for transferring a toner image on the photoreceptor to paper, and the surface thereof is set to be in contact with the surface of the photoreceptor 201. The transfer roller 213 is an elastic roller in which an electrically conductive elastic member is disposed around a shaft formed from an electrically conductive metal. The pressing force applied

to the photoreceptor 201 is 0 to 2,000 g per transfer roller 213 (about 216 mm), desirably 500 to 1,000 g. This was measured on the basis of a product of a spring coefficient and the amount of shrinkage of a spring for pressing the transfer roller 213 to bring into contact with the photoreceptor 201. The contact width with the photoreceptor 201 is about 0.5 mm to 5 mm. The rubber hardness of the transfer roller 213 is 80 degrees or less, desirably 30 to 40 degrees on an Asker C measuring method (measurement by not using a roller shape but using a block piece) basis. In the elastic roller 213, an expandable urethane elastomer to which a lithium salt, e.g., Li20, was added internally so as to adjust the resistance value at 107 Ω (electrodes are disposed on the shaft and the surface, and a voltage of 500 V was applied to them) was used around a shaft having a diameter of 6 mm. The outer diameter of the entire transfer roller 213 was 16.4 mm, and the hardness was 40 degrees on an Asker C basis. The transfer roller 213 was contacted with the photoreceptor 201 by pressing the shaft of the transfer roller 213 with a metal spring. The pressing force was about 1,000 g. For the elastic body of the roller, an elastomer formed from a material, e.g., CR rubber, NBR, Si rubber, or fluororubber, other than the above-described expandable urethane elastomer can also be used. For a conductivity-imparting agent to impart the electrical

conductivity, an electrically conductive substance, e.g., carbon black, other than the above-described lithium salt can also be used.

[0168] Reference numeral 214 denotes an introduction guide formed from an electrically conductive member for guiding transfer paper to the transfer roller 213, and reference numeral 215 denotes a transport guide in which the surface of an electrically conductive member is provided with an insulating coating. The introduction guide 214 and the transport guide 215 are grounded directly or via a resistor. Reference numeral 216 denotes transfer paper, and reference numeral 217 denotes voltage generation power supply for applying a voltage to the transfer roller 213.

[0169] Reference numeral 218 denotes a cleaning blade for scraping off toner remaining after the transfer, reference numeral 219 denotes a cleaning box for storing waste toner, and reference numeral 224 denotes the waste toner. Although an elastic urethane blade was used as the cleaning blade, the same result is obtained by a fur brush applied with a bias or an electrically conductive metal roller.

[0170] The magnetic flux density on the surface of the photoreceptor 201 was 600 Gs. The magnetic force in the inside of the electrode roller 208 was made stronger to improve the transport property. The magnetic pole angle θ of the magnet 202 shown in the drawing was set at 15 degrees.

The diameter of the photoreceptor 201 was 30 mm, and the photoreceptor 201 was used by being rotated at a circumferential speed of 260 mm/s in the direction indicated by an arrow shown in the drawing. The diameter of the electrode roller 208 was 16 mm, and the electrode roller 208 was used by being rotated at a circumferential speed of 40 mm/s in the direction opposite to the movement direction of the photoreceptor 201 (in the direction indicated by an arrow shown in the drawing). The gap between the photoreceptor 201 and the electrode roller 208 was set at 300 μm. The photoreceptor 201 was electrostatically charged to -500 V by the corona electric charger 203 (applied voltage was -4.5 kV, the voltage of the grid 204 was -500V). The resulting photoreceptor 201 was irradiated with the laser light 205 to form an electrostatic latent image. The exposure potential of the photoreceptor 201 at this time was -90 V. The toner 207 was adhered on the surface of the photoreceptor 201 by the magnetic in the toner hopper 206. The photoreceptor 201 was passed before the electrode roller 208. When a non-charged region on the photoreceptor 201 was passed by, an alternating-current voltage (frequency 1 kHz) of 750 V0-p (1.5 kV in peak to peak) superimposed by a direct current voltage of 0 V was applied to the electrode roller 208 by the alternating-current high voltage power supply 210. Thereafter, when the photoreceptor 201 charged

to -500 V with electrostatic latent images written was passed by, an alternating-current voltage (frequency 1 kHz) of 750 V0-p (1.5 kV in peak to peak) superimposed by a direct current voltage of -350 V was applied to the electrode roller 208 by the alternating-current high voltage power supply 210. Consequently, the toner adhered to the electrostatically charged portion on the photoreceptor 201 was recovered with the electrode roller 208, and a toner image with negative and positive reversed was left simply as the image portion on the photoreceptor 201.

[0171] The toner adhered to the electrode roller 208 rotating in the direction indicated by the arrow was scraped by the scraper 211, and was returned into the toner hopper 206 again so as to be used for the next image formation. The thus obtained toner image on the photoreceptor 201 was transferred to the transfer paper 216 with the transfer roller 213, and was fixed thermally with a fixing unit (not shown in the drawing) so as to produce a copied image.

[0172] The image evaluation was performed with respect to the image density and background fog of an image formed at an early stage and an image after a durability test after 10,000 copies. The background fog was determined visually, and a level which caused no practical problem was evaluated as satisfactory (O). When filming occurs on the photoreceptor, the force to transport a postcard is reduced,

and a black dot is generated on the photoreceptor so as to appear as an image noise.

[0173] Images were produced with the above-described electrophotographic apparatus by using the Toner samples A1 to A9. There was no disturbance in horizontal lines, no scattering of toner, no poor transfer, no pollution on the back of the paper, or no hollow defect in characters. Solid black images were uniform, even a line image of 16 lines/mm having a density of 1.4 was reproduced and, therefore an image exhibiting extremely high resolution and high image quality was able to be produced. A high density image having an image density of 1.4 or more was obtained. No background fog was present in the non-image portion. When a long period copy test of 10,000 copies was performed, no toner was adhered to the scraper, no filming of the toner (wax) on the surface of the photoreceptor was present, and copied images with high density and low background fog, the images being compatible to those formed at an early stage, were obtained. The fixing property and the offset resistance were also satisfactory. There was no disturbance in the images under a high humidity. Therefore, it is believed that low resistance substances can be removed uniformly.

[0174] (Example 2) For the carrier, 100 parts of ferrite particles were dipped in a coating resin solution in which 1

part of coating resin is dissolved into 50 parts of xylene and, thereafter, xylene was removed by heating. Furthermore, a heat treatment was performed at a predetermined temperature for a predetermined time, and agglomerate was screened.

[0175] For the contact angle and the dynamic friction coefficient of the coating resin, a präparat was coated with the coating resin solution and this was used as a sample for measurement.

[0176] The sample was prepared by dropping a few drops of coating resin solution on the glass präparat, performing coating by using a glass rod in a manner similar to that in bar coating, and performing a heat treatment under the condition similar to that of the above-described carrier.

[0177] For the contact angle, a contact angle meter (FACE produced by KYOWA INTERFACE SCIENCE CO., LTD.) was used, a droplet of pure water was dropped on the surface of the above-described präparat sample, and the contact angle relative to water was measured.

[0178] For the dynamic friction coefficient, HEIDON Type 14 (produced by HEIDON) was used, and the dynamic friction coefficient was measured with a steel ball indenter.

[0179] For the measurement, the glass präparat sample was placed (on a stage), the steel ball indenter was brought into contact with the sample surface gradually, a weight of

10 g was placed on a pan in an upper portion of the indenter. A load converter was connected, and the stage was moved at a scanning rate of 10 mm/sec, and an indicated value at that time was taken as the dynamic friction coefficient.

[0180] For the measurement of the dynamic friction coefficient relative to a toner, the toner is applied uniformly to a glass plate surface, which has been coated with the resin, on a stage by using a blade, so as to form a thin layer. A glass plate of 18 mm long and 18 mm wide is attached to an indenter attachment portion of the apparatus, a weight of 500 g is placed on the pan in the upper portion of the indenter, a stage is allowed to reciprocate 200 times with a scanning width of 30 mm at a rate of 500 mm/sec, while the toner layer is held between a glass präparat and a cover glass. Subsequently, the glass präparat and the cover glass are temporarily detached from the apparatus, and are attached again to the apparatus after the adhered toner is removed lightly with air. A weight of 10 g was placed on the pan in the upper portion of the indenter, a load converter was connected, and the stage was moved at 10 mm/sec. A value indicated by the apparatus at that time was taken as the dynamic friction coefficient.

[0181] The dynamic friction coefficient of the toner is correlated to the amounts of shaving of the films of the photoreceptor. If the dynamic friction coefficient becomes

0.15 or less, the photoreceptor is not shaved anymore, and disturbance in the image occurs under a high humidity. If it becomes 0.35 or more, a damage to the photoreceptor is increased conversely, and flaw and the like tend to occur.

[0182] Resin coating materials of the carriers are shown in (Table 6), and prototyping conditions and properties of the carriers are shown in (Table 7).

[0183]

[Table 6]

Sample No.	JC1	JC2	JC3
Material	straight silicone resin	straight silicone resin having a phenyl group in a side chain	butyl acrylate resin

[0184]

[Table 7]

Carrier sample	Coating resin material	Ratio	Film thick-ness	Heat treatment temperature	Heat treatment time	Amount of electrically conductive agent	Contact angle	Dynamic friction coefficient with steel ball
CA1	JC1/JC2	8/2	1 µm	180	3 h	8 parts by weight	112°	0.015
CA2	↑	↑	↑	220	↑	↑	107	0.015
CA3	↑	↑	↑	260	↑	↑	103	0.03
CA4	↑	5/5	↑	180	↑	↑	108	0.03
CA5	↑	2/8	↑	180	↑	↑	104	0.05
CA6	↑	↑	↑	220	↑	↑	101	0.06
CA7	↑	↑	↑	260	↑	↑	100	0.08
CA8	JC1/JC3	7/3	↑	180	↑	↑	113	0.015
CA9	↑	5/5	↑	↑	↑	↑	110	0.03
CA10	TC1/JC2/JC3	6/1/3	↑	↑	↑	↑	105	0.05
CA11	↑	6/2/2	↑	↑	↑	↑	102	0.06

[0185] A formulation of a toner to be used in Example is shown in (Table 8).

[0186]

[Table 8]

Binder resin	styrene butyl acrylate copolymer RS1, RS2	100 parts by weight
Pigment	carbon black (MA100S produced by MITSUBISHI CHEMICAL CORPORATION) KETJENBLACK	4 parts by weight 4 parts by weight
Charge controlling agent	Cr alloy azo dye (S34 produced by Orient Chemical Industries, Ltd.)	2 parts by weight
Wax	W1, W2, W3, W4, W5	
Releasing agent	polypropylene (TP32 produced by Sanyo Chemical Industries, Ltd.)	2 parts by weight
External additive	G1 to G4	

[0187] Toner samples and materials used in Example and various properties are shown in (Table 9).

[0188]

[Table 9]

Toner sample No.	Binder resin	Wax	Amount of addition of wax (parts by weight)	External additive	Amount of addition of external additive (parts by weight)	GF	BF	TF	ST/SB
A10	RS2	W1	6	G2	1	0.25	0.15	0.26	1.43
A11	↑	W2	↑	G3	1	0.23	0.17	0.25	1.43
A12	↑	W3	↑	G1	1	0.25	0.18	0.29	1.47
A13	RS1	W3/W4	3/2	G2	1	0.24	0.15	0.25	1.41
A14	↑	W3/W5	3/4	G2/G8	1/1	0.26	0.17	0.28	1.49
A15	↑	↑	↑	G2/G10	1/0.5	0.28	↑	0.30	1.47
A16	RS2	↑	↑	G1/G11	1/0.5	0.27	↑	0.30	1.50
A17	↑	↑	↑	G2/G12	1/1	0.24	↑	0.28	1.53
A18	↑	↑	↑	G2/G14	1/1.2	0.23	↑	0.25	1.56

[0189] Toners and carriers of developing agent samples used in Example and various properties thereof are shown in (Table 10). The external addition treatment conditions were basically the same as the conditions in Example 1. However, a non-magnetic toner was used in the present Example, and the amount of input was specified to be 1.5 kg.

[0190]

[Table 10]

Developing agent sample	Carrier	Toner	Dynamic friction coefficient	Electrostatic charge rising index
D1	CA1	A10	0.18	0.89
D2	↑	A11	0.20	0.90
D3	↑	A12	0.21	0.88
D4	CA7	A13	0.23	1.12
D5	↑	A14	0.24	1.10
D6	↑	A15	0.27	1.20
D7	CA8	A16	0.20	1.01
D8	↑	A17	0.18	1.00
D9	↑	A18	0.16	1.11
D10	CA10	A10	0.18	0.78
D11	↑	A16	0.27	0.77
D12	↑	A18	0.23	0.80

[0191] Fig. 2 is a sectional view showing the configuration of an electrophotographic apparatus used in the present Example 2. The apparatus of the present Example has a configuration in which FP-7742 (produced by Matsushita Electric Industrial Co., Ltd.) copying machine is modified, a two-component developing system is adopted, and a waste toner recycle mechanism is added.

[0192] Reference numeral 220 denotes a developing sleeve, reference numeral 221 denotes a doctor blade, reference

numeral 222 denotes a magnet roll for retaining carriers, reference numeral 223 denotes a carrier, reference numeral 224 denotes a waste toner remaining after transfer, and reference numeral 225 denotes a transport tube for returning the waste toner 224 from the cleaning box 219 to a developing process. The other reference numerals indicate components similar to those in the electrophotographic apparatus shown in Fig. 1. In the configuration, the toner remaining after transfer is scraped off with the cleaning blade 218, and the waste toner 224 temporarily stored in the cleaning box 219 is returned to the developing process with the transport tube 225.

[0193] The image evaluation was performed with respect to the image density and background fog of an image formed at an early stage and an image after a durability test after 10,000 copies. The first 50,000 copies were produced without waste toner recycle, and the following 50,000 copies were produced with the waste toner recycle. The background fog was determined visually, and a level which caused no practical problem was evaluated as satisfactory (O). When filming occurs on the photoreceptor, the force to transport a postcard is reduced, and a black dot is generated on the photoreceptor so as to appear as an image noise.

[0194] Images were produced with the above-described electrophotographic apparatus by using the Toner samples A10

to A18. There was no disturbance in horizontal lines, no scattering of toner, no poor transfer, no pollution on the back of the paper, or no hollow defect in characters. Solid black images were uniform, even a line image of 16 lines/mm having a density of 1.4 was reproduced and, therefore an image exhibiting extremely high resolution and high image quality was able to be produced. A high density image having an image density of 1.4 or more was obtained. No background fog was present in the non-image portion. The fixing strength and the offset resistance were also satisfactory. When a long period copy test of 10,000 copies was performed, no filming of the toner (wax) on the surface of the photoreceptor was present, and copied images with high density and low background fog, the images being compatible to those formed at an early stage, were obtained. There was no disturbance in the images under a high humidity. Therefore, it is believed that low resistance substances can be removed uniformly.

[0195] (Example 3) Fig. 3 is a sectional view showing the configuration of an electrophotographic apparatus for forming a full color image, used in the present Example. In Fig. 3, reference numeral 1 denotes an outer housing of a color electrophotographic printer, and the right end surface side in the drawing is the front thereof. Reference numeral 1A denotes a printer front board, and this front board 1A

can freely be tilted to open as indicated by dotted lines and be raised to close as indicated by solid lines on its hinge axis 1B on the lower hem side of the printer outer housing 1. The front board 1A is tilted and opened to widely expose the inside of the printer for the inspection, maintenance, or the like of the inside of the printer when an intermediate transfer belt unit 2 is attached to or removed from the inside of the printer, paper jam has occurred, and so forth. The intermediate transfer belt unit 2 is designed in such a way that it can be attached or removed in the direction perpendicular to the direction of rotation axis generatrix of the photoreceptor.

[0196] Fig. 4 shows the configuration of the intermediate transfer belt unit 2. The intermediate transfer belt unit 2 includes an intermediate transfer belt 3, a first transfer roller 4 formed from an electrically conductive elastic material, a second transfer roller 5 composed of an aluminum roller, a tension roller 6 for adjusting the tension of the intermediate transfer belt 3, a belt cleaner roller 7 for cleaning toner images remaining on the intermediate transfer belt 3, a scraper 8 for scraping off toner recovered on the cleaner roller 7, waste toner reservoirs 9a and 9b for storing the recovered toner, and a position detector 10 for detecting the position of the intermediate transfer belt 3 in a unit housing 2a. As shown in Fig. 3, the intermediate

transfer belt 3 is attachable to or removable from the predetermined storing position in the printer outer housing 1 by tilting and opening the printer front board 1A as indicated by the dotted lines.

[0197] An electrically conductive filler is kneaded in an insulating resin. A film is formed by using an extruder, and is used as the intermediate transfer belt 3. In the present Example, a film formed from a mixture of 95 parts by weight of polycarbonate resin (for example, lupilon Z300 produced by Mitsubishi Gas Chemical Company, Inc.) as the insulating resin and 5 parts by weight of electrically conductive carbon (for example, KETJENBLACK) was used. The surface thereof was coated with a fluororesin. The thickness of the film was about 350 μm, and the resistance was about 107 to 108 Ω·cm. Here, the film produced by extruding the kneaded mixture of the polycarbonate resin and the electrically conductive filler was used as the intermediate transfer belt 3 to effectively prevent slack due to a long period of use of the intermediate transfer belt 3 and accumulation of electrostatic charge. The surface was coated with the fluororesin to effectively prevent toner from filming the surface of the intermediate transfer belt due to a long period of use.

[0198] The intermediate transfer belt 3 is wound around the first transfer roller 4, the second transfer roller 5, and

the tension roller 6 and is allowed to move in the direction indicated by an arrow. The rollers are formed from endless belt semi-conductive urethane based films having a thickness of 100 μm, and an urethane foam treated to have a low resistance of 107 Ω·cm is formed in the circumferences of the rollers. The circumferential length of the intermediate transfer belt 3 is set at 360 mm, which is a result of adding the length (298 mm) in the longitudinal direction of the largest paper size, A4 size, and a length (62 mm) slightly longer than a half of the circumferential length of a photoreceptor drum (diameter of 30 mm) as described below.

[0199] When the intermediate transfer belt unit 2 is mounted on the printer body, the first transfer roller 4 is pressed by a force of about 1.0 kg to contact a photoreceptor 11 (shown in Fig. 4) with the intermediate transfer belt 3 therebetween, the second transfer roller 5 is pressed to contact with the third transfer roller 12 (shown in Fig. 4), which has the same configuration as that of the first transfer roller 4, with the intermediate transfer belt 3 therebetween. The third transfer roller 12 can be rotated in accordance with the movement of the intermediate transfer belt 3.

[0200] The cleaner roller 7 is a roller in a belt cleaner section for cleaning the intermediate transfer belt 3. In this configuration, an alternating-current voltage is

applied to a metal roller in order to attract the toner electrostatically. This cleaner roller 7 may be a rubber blade or an electrically conductive fur brush to which a voltage has been applied.

[0201] In Fig. 3, four fan-shaped image formation units 17Bk, 17Y, 17M, and 17C for individual colors of black, cyan, magenta, and yellow constitute an image formation unit group 18 and are disposed annularly, as shown in the drawing, in the center of the printer. Each of the image formation units 17Bk, 17Y, 17M, and 17C can freely be attached to and removed from a predetermined position of the image formation unit group 18 by opening a printer upper board 1C on its hinge axis 1D. When the image formation units 17Bk, 17Y, 17M, and 17C are incorporated in the printer properly, the mechanical driving systems and the electrical circuit systems on both sides of the image formation units and the printer are connected via inter-coupling members (not shown in the drawing) and are mechanically and electrically integrated.

[0202] The image formation units 17Bk, 17C, 17M, and 17Y disposed annularly are supported by a support (not shown in the drawing), and the whole is driven by a movement motor 19 serving as a movement device, and can be rotationally moved around a cylindrical shaft 20 that is fixed and not rotated. Each of the image formation units can be positioned at an

image formation position 21 opposed to the second transfer roller 4 supporting the above-described intermediate transfer belt 3 one after another by rotational movement. The image formation position 21 is an exposure position by the signal light 22 as well.

[0203] Since the image formation units 17Bk, 17C, 17M, and 17Y have the same constituent members except the developers contained therein, for the sake of simplified explanation, only the image formation unit 17Bk for black will be described, and explanations of the units for the other colors will be omitted.

[0204] Reference numeral 35 denotes a laser beam scanner section disposed in a lower portion in the printer outer housing 1, and is composed of a semiconductor laser, although not shown in the drawing, a scanner motor 35a, a polygon mirror 35b, a lens system 35c and the like. The pixel laser signal light 22 corresponding to a time series electric pixel signal for image information from the laser beam scanner section 35 passes through an optical path window 36 formed between the image formation units 17Bk and 17Y so as to be incident to a mirror 38 fixed in the shaft 20 through a window 37 opened in a part of the shaft 20, and is reflected to travel through an exposure window 25 in the image formation unit 17Bk located at the image formation position 21 and enters the image formation unit 17Bk

substantially horizontally. Then, the light passes through a path between a developer reservoir 26 and a cleaner 34, which are disposed in upper portion and lower portion in the image formation unit, and is incident to an exposure portion on the left side surface of the photoreceptor 11 so as to perform scanning and exposure in the generatrix direction.

[0205] Since a gap between the adjacent image formation units 17Bk and 17Y is used as the optical path from the optical path window 36 to the mirror 38, there is substantially no space that is wasted in the image formation unit group 18. Since the mirror 38 is disposed at the center of the image formation unit group 18, the mirror can be composed of a single fixed mirror, so that the configuration is simple and easy for registering and the like.

[0206] Reference numeral 12 denotes the third transfer roller disposed inside the printer front board 1A and above a paper feeding roller 39. A paper transport path is formed in a nip portion where the intermediate transfer belt 3 and the third transfer roller 12 are pressure-contacted so that the paper is fed from the paper feeding roller 39 disposed below the printer front board 1A.

[0207] Reference numeral 40 denotes a paper feeding cassette disposed protruding outwardly in a lower hem side of the printer front board 1A, and a plurality of sheets of

paper S can be set therein simultaneously. Reference numerals 41a and 41b denote paper transport timing rollers, reference numerals 42a and 42b denote a pair of fixing rollers disposed in an upper portion in the printer, reference numeral 43 denotes a paper guide board disposed between the third transfer roller 12 and the pair of fixing rollers 42a and 42b, reference numerals 44a and 44b denote a pair of paper ejecting rollers disposed on the paper outlet side of the pair of fixing rollers 42a and 42b, reference numeral 45 denotes a fixing oil reservoir for storing silicone oil 46 to be supplied to the fixing roller 42a, and reference numeral 47 denotes an oil supply roller for applying the silicone oil 46 to the fixing roller 42a.

[0208] Each of the image formation units 17Bk, 17C, 17M, and 17Y and the intermediate transfer belt unit 2 includes a waste toner reservoir.

[0209] The operations will be described below. First, for the image formation unit group 18, as shown in Fig. 3, the image formation unit Bk for black is located at the image formation position 21. At this time, the photoreceptor 11 is opposed to and in contact with the first transfer roller 4 with the intermediate transfer belt 3 therebetween.

[0210] In the image formation process, signal light for black is input into the image formation unit 17Bk by the laser beam scanner section 35, and images are formed with a

black toner. The image formation rate (60 mm/s, which is equal to the circumferential speed of the photoreceptor) in the image formation unit 17Bk is set at the same rate as the movement rate of the intermediate transfer belt 3. Therefore, upon the image formation, the black toner images are transferred to the intermediate transfer belt 3 by the function of the first transfer roller 4. At this time, a direct-current voltage of +1 kV is applied to the first transfer roller. Immediately after all the black toner images are transferred, the whole of the image formation units 17Bk, 17C, 17M, and 17Y is driven by the movement motor 19 so as to rotationally move as the image formation unit group 18 in the direction indicated by an arrow shown in the drawing. Exactly 90 degrees rotation is performed and, thereby, the image formation unit 17C is stopped at the image formation position 21. During this movement, portions other than the photoreceptor in the image formation unit, e.g., the toner hopper 26 and the cleaner 34, are positioned inward from the rotating curve of the end of the photoreceptor 11, so that the intermediate transfer belt 3 is never brought into contact with the image formation units.

[0211] After the image formation unit 17C reaches the image formation position 21, in the same manner as described above, the laser beam scanner section 35 inputs signal light 22 with signals for cyan into the image formation unit 17C, and

cyan toner images are formed and transferred. The intermediate transfer belt 3 has rotated once by this point, and the timing at which the signal light for cyan is written is controlled in such a way that the following cyan toner images are in registration with the black toner images that have been transferred previously. During this period, the third transfer roller 12 and the cleaner roller 7 are at a small distance from the intermediate transfer belt 3 so as not to disturb the toner images on the transfer belt.

[0212] The same operations as in the above description was performed for magenta and yellow, and color images obtained by superimposing the toner images of four colors in registration were formed on the intermediate transfer belt 3. After the last transfer of yellow toner images, the toner images of four colors were transferred collectively to the paper fed from the paper feeding cassette 40 by function of the third transfer roller 12 while the timing was provided. At this time, the second transfer roller 5 was grounded, and a direct-current voltage of +1.5 kV was applied to the third transfer roller 12. The toner images transferred to the paper were fixed by the pair of fixing rollers 42a and 42b. Thereafter, the paper was ejected through the pair of ejecting rollers 44a and 44b to the outside of the apparatus. Toner that has not been transferred and remains on the intermediate transfer belt 3 was cleaned away by the

function of the cleaner roller 7 for the next image formation.

[0213] The operation in a single color mode will be described below. In the single color mode, an image formation unit for a predetermined color is moved to the image formation position 21. Then, in the same manner as that described above, images for the predetermined color are formed and transferred to the intermediate transfer belt 3. In this case, after the transfer, the operation is proceeded, and the images are transferred to the paper fed from the paper feeding cassette 40 by the third transfer roller 12 and is fixed as it is.

[0214] In the present apparatus, the image formation unit has a structure using the developing methods described in Examples 1 and 2. However, other image formation units having a structure using a conventional developing method can also be used.

[0215] Thermal properties of polyester resins serving as the binder resins used in the present Example are shown in (Table 11).

[0216]

[Table 11]

Binder resin	Tg	Mn	Mw	Mz	Mw/Mn	Mz/Mn	Tm	Ti
RM1	60.7	3100	16000	62000	5.2	20	108	91
RM2	55.7	4200	22000	61000	5.2	14.5	105	86
RM3	62.3	2700	31000	570000	11.6	210	114	93

[0217] A formulation of a toner to be used in the present Example is shown in (Table 12).

[0218]

[Table 12]

Binder resin		polyester resin RM1, RM2, RM3	100 parts by weight
Material	Black	carbon black (#44 produced by MITSUBISHI CHEMICAL CORPORATION)	5 parts by weight
	Yellow	benzidine based yellow pigment	5 parts by weight
	Magenta	azo pigment	5 parts by weight
	Cyan	copper phthalocyanine pigment	5 parts by weight
Charge controlling agent		salicylic acid based salt(E-84 produced by Orient Chemical Industries, Ltd.)	2 parts by weight
Wax		W1, W2, W3	
External additive		G1 to G14	

[0219] Toner samples and materials used in the present Example and various properties are shown in (Table 13).

[0220]

[Table 13]

Toner sample No.	Binder resin	Wax	Amount of addition of wax (parts by weight)	External additive	Amount of addition of external additive (parts by weight)	GF	BF	TF	ST/SB
A20	RM1	W1	8	G2	1	0.25	0.17	0.28	1.40
A21	↑	↑	↑	G4	1	0.20	0.17	0.22	1.45
A22	RM2	W2	↑	G2/G8	1/1	0.26	0.15	0.29	1.48
A23	↑	↑	↑	G4/G9	1/1.5	0.23	0.15	0.26	1.50
A24	RM3	W3	↑	G4/G12	1/1	0.21	0.16	0.23	1.52
A25	↑	↑	↑	G2/G13	1/1	0.25	0.16	0.29	1.53

[0221] Images were produced with the above-described electrophotographic apparatus by using the Toner samples produced as described above. There was no disturbance in horizontal lines, no scattering of toner, or no hollow defect in characters. Solid black images were uniform, even a line image of 16 lines/mm having a density of 1.4 was reproduced and, therefore an image exhibiting extremely high resolution and high image quality was able to be produced. A high density image having an image density of 1.4 or more was obtained. No background fog was present in the non-image portion. Furthermore, in a long period durability test of 5,000 copies, both the fluidity and the image density exhibited small changes and, therefore, stable properties were exhibited. In the transfer as well, hollow defect was at a level which caused no practical problem, and a transfer efficiency of 90% or more was obtained. The filming of toner (releasing agent) on the photoreceptor and the intermediate transfer belt was at a level which caused no practical problem.

[0222] There was no disturbance in the images under a high humidity. The transmittance when a solid image with the amount of adhesion of 0.7 mg/cm^2 or more was fixed to the OHP paper at 155°C with a fixing unit without applying oil and the offset property at high temperatures were evaluated as shown in (Table 14). The process rate was 100 mm/sec,

and the transmittance of the light of 700 nm was measured with a spectrophotometer U-3200 (produced by Hitachi, Ltd.). The results were satisfactory for practical use.

[0223]

[Table 14]

Toner sample	High temperature offset	Transmittance
A20	no occurrence up to 180°C	90%
A21	no occurrence up to 185°C	90%
A22	no occurrence up to 180°C	89%
A23	no occurrence up to 185°C	90%
A24	no occurrence up to 195°C	86%
A25	no occurrence up to 190°C	85%

[0224]

[Advantages] As described above, according to the present invention, a binder resin having a wide molecular weight distribution is used in order to respond to developing process rates in a wide range and, in addition, a polyethylene wax or a vegetable wax having specific properties is added in order to increase the penetrability into the paper and bring the fixed image surface into a low friction state. Furthermore, the materials and the manufacturing conditions are set in such a way that the dynamic friction coefficient of the external additive to be added to the toner, the dynamic friction coefficient of a toner base before performing an external addition treatment, the dynamic friction coefficient of the toner after performing an external addition treatment, the specific

surface area of the toner base before performing an external addition treatment, and the specific surface area of the toner after performing the external addition treatment satisfy the specific relationships, so that the blade-cleaning property is made excellent while the fixing property and the offset resistance are satisfied, and foreign matters, that is, low resistance substances on the photoreceptor, can be removed effectively. The friction coefficient and the contact angle of the coating film of the carrier are specified and, thereby, in the two-component developing, the mixing property with the toner is made uniform to improve electrostatic charge property, and in particular, an occurrence of background fog due to delay in the trackability in electrostatic charging when the toner is replenished rapidly can be prevented. Furthermore, a toner having an excellent waste toner recycling property and an excellent transfer property in the roller transfer and the intermediate transfer can be obtained.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a sectional view showing the configuration of an electrophotographic apparatus used in Example 1 of the present invention, wherein the developing system is a magnetic single-component developing system.

[Fig. 2] Fig. 2 is a sectional view showing the configuration of an electrophotographic apparatus used in

Example 2 of the present invention, wherein the developing system is a two-component developing system.

[Fig. 3] Fig. 3 is a sectional view showing the schematic configuration of a color electrophotographic apparatus used in Example 3 of the present invention.

[Fig. 4] Fig. 4 is a sectional view showing the configuration of the intermediate transfer belt unit shown in Fig. 3.

[Fig. 5] Fig. 5 is a sectional view showing the schematic configuration of a color electrophotographic apparatus.

[Reference Numerals]

2: intermediate transfer belt unit

3: intermediate transfer belt

4: first transfer roller

5: second transfer roller

6: tension roller

11: photoreceptor

12: third transfer roller

17Bk, 17C, 17M, 17Y: image formation unit

18: image formation unit group

21: image formation position

22: laser signal light

35: laser beam scanner section

38: mirror

201: photoreceptor

202: fixed magnet included in photoreceptor

203: corona electric charger

204: grid electrode

206: toner hopper

207: magnetic single-component toner (developer)

208: electrode roller

209: magnet disposed in electrode roller

211: scraper

213: transfer roller

214: introduction guide

215: transport guide

216: transfer paper

218: cleaning blade

219: cleaning box

220: developing sleeve

221: doctor blade

222: magnet roll

224: waste toner

225: waste toner transport tube

FIG. 1

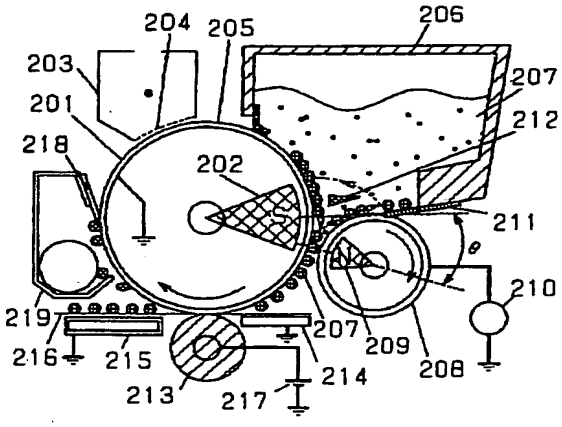


FIG. 2

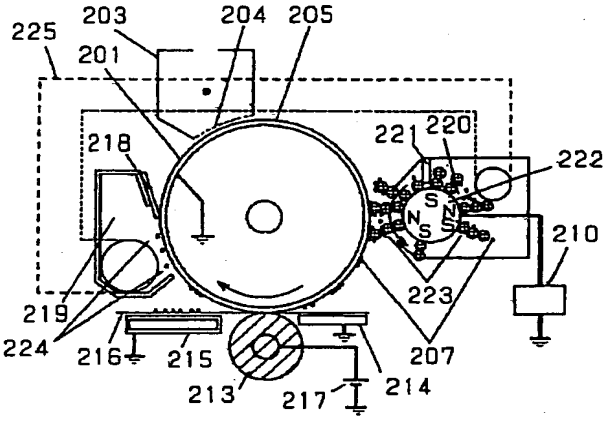


FIG. 3

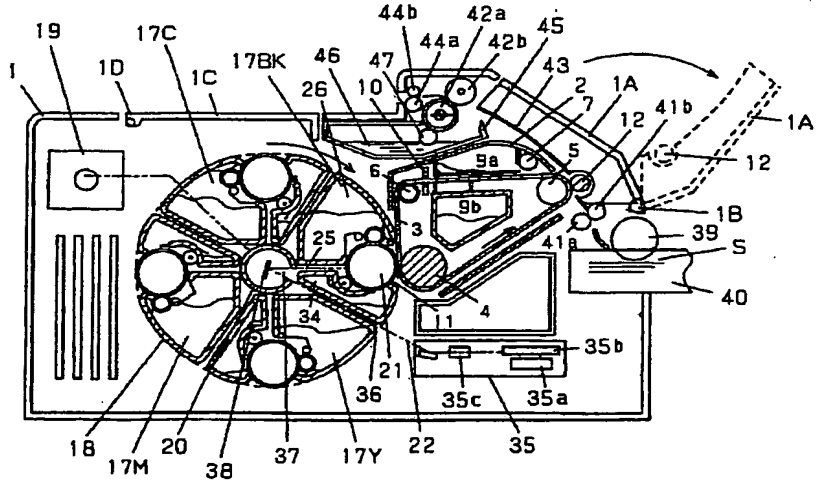


FIG. 4

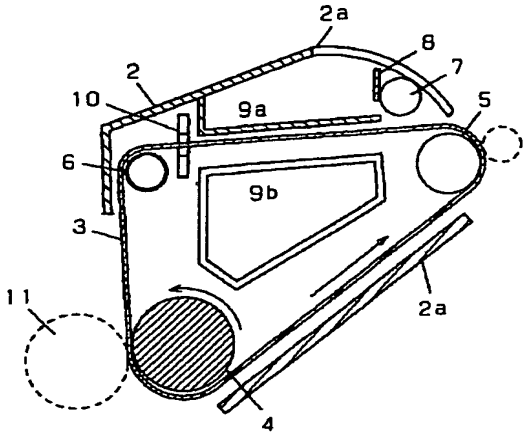


FIG. 5